TITLE SYNTHESIS, STRUCTURE AND CHEMICAL STUDIES OF CATIONIC M(IV) SPECIES WHERE M=TI, ZR, HF AND SN

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SYNTHESIS, STRUCTURE AND CHEMICAL STUDIES OF CATIONIC M(IV) SPECIES

where M = Ti, Zr, Hf and Sn

by

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Declaration - All of the work described in this thesis is original and was, except where otherwise stated, carried out by the author.

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Parts of the work described in this thesis have been published in the scientific literature:

Crown Ether Complexation of Titanium: Synthesis and Structural Characterisation of a Cationic Oxygen-Bridged Titanium (IV) Dimer."
Gerald R. Willey, Janet Palin and Nathaniel W. Alcock

J.Chem.Soc.,Dalton Trans, 1992 1117

A study of the reactions of [9]aneS$_3$ with early transition metal halides: synthesis and structure of [Fe([9]aneS$_3$)$_2$][Sb$_2$Cl$_8$], [9]aneS$_3$ = 1,4,7-trithiacyclononane.
Gerald R. Willey, Janet Palin, Miles T. Lakin and Nathaniel W. Alcock

Transition Met. Chem., 1994 **19** 187.

Crown Thioether Chemistry of Sn (IV): formation and crystal and molecular structures of 3SnCl$_4$·2([9]aneS$_3$) (I) and 2SnCl$_4$·([18]aneS$_6$) (II), [9]aneS$_3$ = 1,4,7-trithiacyclononane, [18]aneS$_6$ 1,4,7,10,13,16-hexathiacyclooctadecane
Gerald R. Willey, Adam Jarvis, Janet Palin and William Errington.

J.Chem.Soc., Dalton Trans., 1994 225.

Controlled hydrolysis reactions of solvated [TiCl$_n$]$^{(4-n)+}$ species. Crystal and molecular structures of [Mg(MeCN)$_6$][{TiCl$_4$(MeCN)}$_2$(μ-O)]·4MeCN (I) and [TiCl$_2$(MeCN)$_2$(μ-O)]$_4$·2MeCN (II).
Gerald R. Willey, Janet Palin and Michael G. B. Drew,

J.Chem.Soc., Dalton Trans. 1994 In press.

ABBREVIATIONS

LIGANDS

MeCN = acetonitrile

THF = tetrahydrofuran

DMF = dimethylformamide

DMSO = dimethyl sulphoxide

Ac = Acetyl

Cp = cyclopentadienyl

Cp^* = pentamethylcyclopentadienyl

$Cp^{\blacksquare}$ = $1,3\text{-}(t\text{-}Bu)_2Cp$

acac = acetylacetonate anion

en = ethylenediamine

hmpa = hexamethylphosphoric triamide

12-C-4 = 1, 4, 7, 10-tetraoxacyclododecance

15-C-5 = 1, 4, 7, 10, 13-pentaoxacyclopentadecane

18-C-6 = 1, 4, 7, 10, 13, 16-hexaoxacyclooctadecane

9-S-3 = 1, 4, 7-trithiacyclononane

12-S-4 = 1, 4, 7, 10-tetrathiacyclododecane

15-S-5 = 1, 4, 7, 10, 13-pentathiacyclopentadecane

18-S-6 = 1, 4, 7, 10, 13, 16-hexthiacyclooctadecane

1-aza-12-C-4 = 1, 4, 7-trioxa-10-azacyclododecane

1-aza-15-C-5= 1, 4, 7, 10-tetraoxa-13-azacyclopentadecane

1-aza-18-C-5 = 1, 4, 7, 10, 13-pentaoxa-16-azacyclooctadecane

OEP = 2,3,7,8,12,13,17,18-octaethylporphinato dianion

$OEPMe_2$ = α-γ-dimethyl-α-γ-dihydrooctaethylporphinato dianion

PC = $(C_{32}H_{16}N_8)^{2-}$ = phthalcyaninato dianion

H_2tmtaa = 6,8,15,17-tetramethyl-5,14-dihydro-5,9,14,18-tetraazadibenzo-[a,h]-cyclotetradecene

Salen = salicyclaldimine(ethylenediamine)

tet = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane

ABSTRACT

The reactions of the Lewis acid $SbCl_5$ with MCl_4 (M=Ti, Zr, Hf and Sn) have allowed the isolation of the hexachloroantimonate(V) salts $[MCl_3L_n][SbCl_6]$, where M=Ti, Sn, n=3, L=MeCN and M=Zr, Hf, n=4, L=1,4-dioxane and $[TiClL_7][SbCl_6]_3$, L=MeCN with full spectroscopic characterisation. Other routes to the formation of the cationic species $[TiCl_3L_3]^+$ have been investigated, including halide abstraction using the reagents $AgBPh_4$, $NaBPh_4$ and $AgBF_4$.

Reactions of $[TiCl_3(MeCN)_3][SbCl_6]$ with the crown ether ligands, 1,4,7,10-tetraoxocyclododecane (12-C-4), 1,4,7,10,13-pentaoxocyclopentadecane (15-C-5) and 1,4,7,10,13,16-hexaoxocyclooctadecane (18-C-6) have been studied. The products obtained are not the expected direct adducts *ie.* ligand exchange following replacement of MeCN by crown ether but rather the μ-oxo-bridged $[\{TiCl(\mu\text{-}O)(12\text{-}C\text{-}4)\}_2][SbCl_6]_2\cdot 2CH_2Cl_2$ and $[\{TiCl(\mu\text{-}O)(15\text{-}C\text{-}5)\}_2][SbCl_6]_2$. The 12-crown-4 species was studied by X-ray diffraction methods. Plausible routes to their formation are forwarded. In the case of 18-C-6, the hydrolysis product, $[H_3O(18\text{-}C\text{-}6)][SbCl_6]$ was isolated.

Reactions of the neutral MCl_4 (M= Ti, Zr, Hf and Sn) with crown thioethers, 1,4,7-trithiacyclononane (9-S-3), 1,4,7,10-tetrathiacyclododecane, (12-S-4), 1,4,7,10,13-pentathiacyclopentadecane, (15-S-5) and 1,4,7,10,13,16-hexathiacyclohexadecane, (18-S-6) have been studied. The reactions led to the isolation of $[TiCl_4(9\text{-}S\text{-}3)]$, $[SnCl_3(9\text{-}S\text{-}3)]_2[SnCl_6]$ and $2SnCl_4\cdot 18\text{-}S\text{-}6$. The latter two compounds were characterised by X-ray diffraction methods. Reaction of the compound $[TiCl_3(MeCN)_3][SbCl_6]$ with the crown thioether 9-S-3 was unsuccesful.

Extending the choice of ligands to include macrocyclic azaoxacrown ethers 1, 4, 7-trioxa-10-azacyclododecane (1-aza-12-crown-4), 1, 4, 7, 10-tetraoxa-13-azacyclopentadecane (1-aza-15-crown-5) and 1, 4, 7, 10, 13-pentaoxa-16-azacyclooctadecane (1-aza-18-crown-6), led to the isolation of complexes of the type $[H_2L]_2[TiCl_5(H_2O)]_2\cdot H_2O\cdot MeCN$ where L=appropriate azaoxacrown.

Controlled hydrolysis reactions of solvated $[TiCl_n]^{(4-n)+}$ species have been studied as a route to titanoxanes. The *bis*-adduct $TiCl_4(MeCN)_2$ provides the neutral tetranuclear μ-oxo compound $[TiCl_2(MeCN)_2(\mu\text{-}O)]_4$ whilst the pentachloroanion in the form of $[Mg(MeCN)_6][TiCl_5(MeCN)]_2$ yields the μ-oxo-dititanium anion $[\{TiCl_4(MeCN)\}_2(\mu\text{-}O)]_4^{2-}$. Both products were the subject of X-ray structure examination.

During an exchange programme involving the University of Alcalá de Henares, Madrid, the reaction of Cp^*TiCl_3 (where $Cp^* = \eta^5$-(1,3-ditert-C_4H_9)Cp) with the carboxylic acid *p*-toluic acid was studied. Following *in situ* formation of Cp^*TiMe_3, reaction with 3 equivalents of *p*-toluic acid afforded crystals of $[Cp^*Ti(\mu\text{-}O)(C_6H_4CH_3CO_2)]_2$. The compound was structurally characterised by X-ray diffraction.

CHAPTER 1

INTRODUCTION TO THE CHEMISTRY OF Ti, Zr, Hf AND Sn(IV)

INTRODUCTION

The Chemistry and Properties of Titanium[1, 2, 3]

Titanium is the most naturally occurring transition metal after iron and widely distributed through the earths crust. Despite this, the industrial potential was only developed in this century, owing to the arrival of economically viable extraction methods. The most important method for producing the metal is the Kroll process.[4] In the initial stage the ore, ilemenite $FeTiO_3$ or rutile TiO_2, is heated with carbon and Cl_2 to yield $TiCl_4$, which is collected by distillation. (Eqn 1)

$$2FeTiO_3 + 7Cl_2 + 6C \rightarrow 2TiCl_4 + 2FeCl_3 + 6CO \qquad (1)$$

The second stage utilises magnesium as a reducing agent in an atmosphere of argon. (Eqn 2)

$$TiCl_4 + 2Mg \rightarrow Ti + 2MgCl_2 \qquad (2)$$

Finally, the magnesium chloride is removed either by volatilization or extraction with water and dilute HCl. The remaining titanium metal is cast into ingots.

Of the compounds formed by titanium the oxide TiO_2 is by far the most important. The value placed on TiO_2 stems from its exceptionally high refractive index. As a consequence, it is of great demand in the surface coating industries, where it is used to produce films of high opacity.[5]

Oxidation States

Titanium has a valence shell configuration of $3d^2 4s^2$. The most stable and most common oxidation state is +IV. However, the element also exhibits a range of lower oxidation states (Ti -II, -I, 0, +II, +III). The latter states are invariably unstable to oxidation and are usually only found with π - acid ligands.[6]

This discussion will be limited to the highest oxidation state (IV) as it is the most relevant to the work described in this thesis. The energy for the removal of all four valence electrons is so high, the Ti^{4+} ion is thought not to exist. As a consequence of the high ionisation potential and high polarising ability of such a species the majority of Ti(IV) compounds have polar covalent bonds.

Tetrahalides

The four halides are readily accessible and chemically very versatile. The most usual method of preparing $TiCl_4$ is treatment of the dioxide with chlorine in the presence of a reducing agent (carbon) at high temperature, 1000°C. The remaining tetrahalides can be conveniently prepared from the tetrachloride by its addition to the respective hydrogen halide.

Coordination Chemistry of Titanium

This ease of preparation and strong Lewis acidity makes TiX_4 ideal starting materials for other titanium compounds. Being strong Lewis acids they readily form addition compounds of the type $TiX_4(L)_2$, $[TiX_4(L)]_2$ and $TiX_4(B)$ with a variety of ligands, L=monodentate, B=bidentate ligand. The relative acceptor strengths of the halides vary along the series Cl > F > Br > I. The surprising placement of fluorine arises because TiF_4 exists as a strongly bonded, highly stable fluoro-bridged polymer which is not easily penetrated by potential donor

species. Relatively few adducts are reported for the tetraiodide as might be expected from its position in the series; [TiI_4(3,3'dimethylacetylacetone)][7] provides a rare example.

Examples of *bis* adducts are listed in Table 1.

Table 1. Titanium Adducts of the Type $TiX_4(L)_2$

Adduct	Ref
$TiCl_4(hmpa)_2$	8
$TiCl_4[(Me_3Si)_2N(C_6H_4)CN]_2$	9
$TiCl_4(NCH)_2$	10
$TiCl_4(L)_2$ L = 3,4-benzoquinoline, benzofuroxane	 11 12
$TiF_4(L)_2$ L = 3,4-benzoquinoline, 5,6-benzoquinoline	 13 13

The adducts are easily isolated, often following reaction of TiX_4 with an excess of the appropriate ligand in a non-coordinating solvent. The octahedral six coordinate complexes, $TiX_4(L)_2$, can exhibit the *cis* or *trans* configuration depending on the particular ligands involved. Infrared examination is usually the most readily accessible method of determining the spatial arrangement of the ligands. The *cis*-$TiX_4(L)_2$ compounds exhibit four ν(Ti-X) stretching modes whilst *trans*-$TiX_4(L)_2$ (D_{4h}) compounds differ markedly, displaying only one ν(Ti-X) stretching band. As expected those compounds with bulky ligands favour a *trans* placement. In keeping with this, IR evidence for $TiF_4(L)_2$ L=3,4-benzoquinoline is consistent with a *trans* octahedral geometry.[13]

$[TiX_4(L)]_2$ Complexes

The low solubility of $[TiF_4(L)]_2$ adducts in organic solvents implies they exist as fluorine bridged polymers. In contrast, the tetrachloride species commonly dimerise through chloro-bridges. Several examples which have been structurally characterised are listed in Table 2.

Table 2. Titanium Adducts of the Type $[TiX_4(L)]_2$

Adduct	Ref
$[TiCl_4(CH_3NO_2)]_2$	14
$[TiCl_4(EtCO_2C_6H_4OCH_3)]_2$	15
$[TiCl_4(NCCO_2Et)]_2$	16
$[TiCl_4(C_4H_8O)]_2$	17
$[TiCl_4(COC_4H_5CH_3)]_2$	18

The latter complex which is the most contemporary of the above examples was isolated by Quinkert *et al*[18] in 1992 and its structure is depicted in Figure 1.

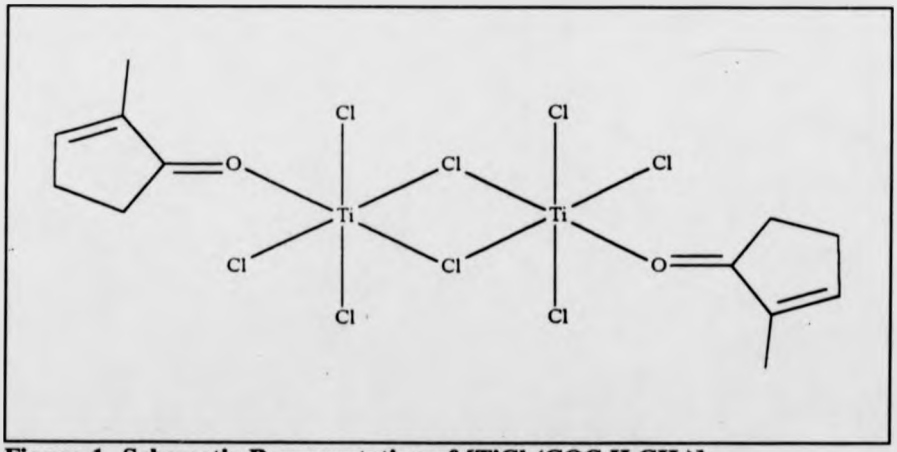


Figure 1. Schematic Representation of $[TiCl_4(COC_4H_5CH_3)]_2$

Thewalt *et al*[19] have shown that the ligand S_4N_4 is also able to bridge two titanium centres via nitrogen chelation in the compound $[TiCl_4(S_4N_4)]_2$. (Figure 2.)

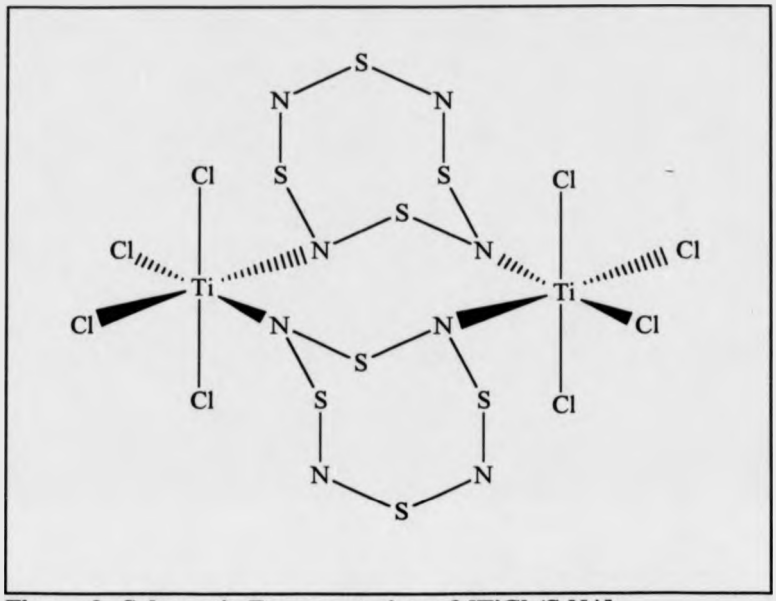


Figure 2. Schematic Representation of $[TiCl_4(S_4N_4)]_2$

$[TiCl_4(B)]$ Complexes (B = Bidentate Ligand)

Many bidentate amide ligands, *N,N'*-dimethyloxamide, *N,N'*-diethyloxamide, *N,N'*-dimethyldithiooxamide, *N,N'*-diethyldithiooxamide and *N,N'*-diethylmalonamide react with $TiCl_4$ to give yellow or orange $TiCl_4(B)$ complexes. From the magnitude of the shifts in the ligand IR bands, ν(C-N) and ν(C-E) (where E = donor atom) following complexation, bidentate O,O'-, or S,S'-attachment of the amide ligands was inferred. Surprisingly this evidence also indicates that the S-donor ligands are more strongly bound to titanium than the corresponding O-donor set.[20] Structural elucidation of $[TiCl_4\{o\text{-}C_6H_4(CO_2Pr)_2\}]$ by Sobota *et al*[21] using X-ray diffraction methods reveals a *cis*-bidentate ligand

attachment typical for the $TiX_4(B)$ compounds. (Figure 3.)

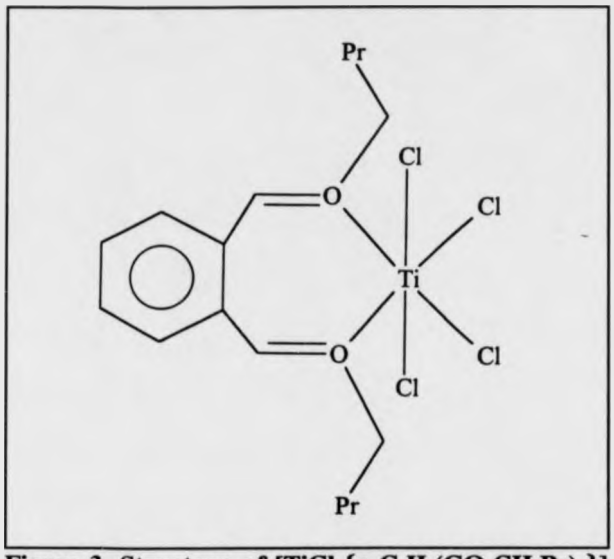


Figure 3. Structure of $[TiCl_4\{o\text{-}C_6H_4(CO_2CH_2Pr)_2\}]$

Coordination Numbers Other than Six

Although titanium(IV) complexes are mostly six coordinate with an octahedral geometry, other structural arrangements are observed based on 5, 7 and 8-fold coordination. Relatively few five coordinate species are known; the monomer $[TiCl_4N(CH_3)]$[22] is a rare example. Seven coordinate titanium atoms are seen in the complexes formed between $TiCl_4$ and (*o*-dimethylarsinophenyl)methylarsine and tris-1, 1, 1-(dimethylarsinomethyl)ethane.[23] Further expansion of the coordination sphere is achieved with other arsenic donor ligands. The potentially bidentate diars, $[o\text{-}C_6H_4(AsMe_2)_2]$, reacts with $TiCl_4$ to yield the mononuclear $TiCl_4(diars)_2$, containing an eight coordinate titanium.[24]

Although other eight coordinate titanium compounds are known, such as $[Ti(NO_3)]_4$, they do not contain a titanium-halide bond.[25]

Chemistry of Zirconium and Hafnium

The conspicuous similarity of these two elements embraces most aspects of their chemistry and is due to the close correspondence of both their atomic and ionic radii: 1.45/0.86 Å for Zr and Zr^{4+}, 1.44/0.85 Å for Hf and Hf^{4+} respectively.[26] The unexpected constriction is attributed to the lanthanide contraction.

The larger size of these elements (Ti«Zr ≈ Hf) often accounts for the disparity seen with some titanium compounds. For example, the oxide ZrO_2 is more basic than TiO_2 as the larger size reduces the polarising power of zirconium.

Tetrahalides

All eight tetrahalides are known. They are chemically versatile (especially the chlorides), being starting materials for subsequent chemical studies.[27]

In the gas phase the halides MCl_4, MBr_4 and MI_4 are tetrahedral monomers, becoming polymeric in the solid state. The polymeric species consist of zigzag chains of $[MX_6]$ units.[26]

Coordination Chemistry

When analogous ZrX_4 and HfX_4 coordination compounds are available they are similar in many respects, with only small differences in solubility and volatility. As with $TiCl_4$, tetrachlorides of the heavier congeners also act as Lewis acids forming addition compounds with a variety of common donor ligands. The nature of these adducts parallels the trend seen in those of titanium, in that compounds containing oxygen donors are reported with greater frequency than those with nitrogen or sulphur donor ligands. The most noticeable disparity with the first group member is that of coordination number. The heavier elements have a greater tendency to expand their coordination sphere, commonly exhibiting a

coordination number of eight, but five, six, seven and nine have also been noted.

Adducts of the Type $MX_4(L)$ and $MX_4(L)_2$

Zirconium and hafnium tetrahalides react with many O-donor ligands such as ethers, aldehydes, ketones and esters affording adducts of the type $MX_4(L)$ and $MX_4(L)_2$, examples of which include: $ZrCl_4$(1,4-dioxane),[28] $HfCl_4$(1,4-dioxane),[28] $ZrCl_4(Me_2O)_2$,[28] $HfCl_4(Me_2O)_2$,[28] $ZrCl_4(DMF)_2$[29] and $ZrCl_4(MeCOBu^t)$.[30]

Synthesis of the 1:1 adducts is achieved following strict adherence to equimolar reagent quantities whilst the 1:2 adducts are obtained through either using two equivalents or an excess of the ligand. Infrared evidence suggests many of the 1:2 adducts *eg.* $ZrCl_4(EtOAc)_2$[31] incorporate a *cis* octahedrally coordinated metal centre. Similar infrared evidence is available for the adducts containing N-donor ligands. In a number of cases this has been corroborated through structural elucidation as with *cis*-$ZrCl_4(NMe_3)_2$[32] and *cis*-$ZrBr_4(NMe_3)_2$[32]. A *cis* ligand arrangement is more common with ZrX_4 (X=Cl, Br) and $HfCl_4$ than for $TiCl_4$ as the larger metal size reduces the steric interaction between bulky ligands attached to the metal centre. Nevertheless, there are exceptions as structural evidence suggests the addition compound $ZrCl_4(py)_2$[33] has a *trans* ligand geometry. Despite ZrX_4 and HfX_4 being typecast hard Lewis acids several adducts with sulphur donor ligands have been observed. The compounds $ZrCl_4(Me_2S)_2$[34], $MCl_4(THT)_2$ (M=Zr or Hf) THT = tetrahydrothiophene[35], $ZrCl_4$(1,4-thioxane)$_2$[36] and $ZrCl_4(MeSCH_2CH_2SMe)_2$[37] are examples of adducts containing S-donor ligands. IR evidence for the latter compound is consistent with an eight coordinate structure arising from bidentate chelation of the metal centre. The inclusion of bidentate ligands in the coordination sphere often increases the coordination

number to eight, affording compounds of either dodecahedral or square antiprismatic geometry. However there are deviations from these ideal geometries, as the adduct formed between $ZrCl_4$ and the ligand 2,2' bi-thiazoline ($C_6H_8N_2S_2$) is intermediate between an ideal dodecahedron and an ideal square anti-prism.[38]

$[MX_4(L)]_2$ Adducts

Although halide bridged compounds containing zirconium and hafnium are sparse, several examples have been structurally characterised. Examples include; $[ZrCl_4(EtOAc)]_2$,[39] $[ZrCl_4(CH_3OCCH_3CO)]_2$[40] and $[ZrCl_4(MeCN)]_2$[41] which is shown in Figure 4.

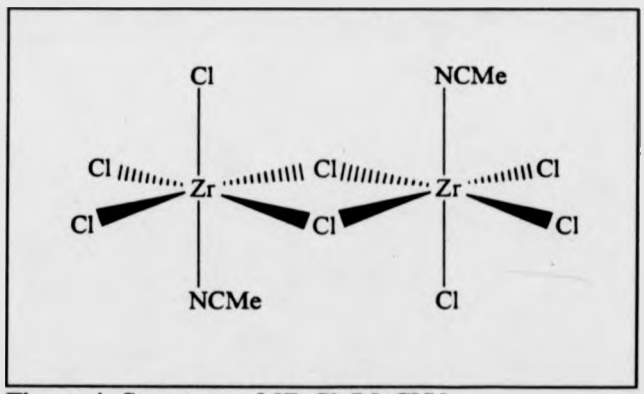


Figure 4. Structure of $[ZrCl_4(MeCN)]_2$

On the basis of IR and Raman spectroscopic data, a similar dimeric chloro-bridged structure has been proposed for the 1:1 adduct formed between $ZrCl_4$ and cyanogen iodide.[42]

Coordination Numbers Other than Six

The complexing properties of the potentially tridentate ligand, triarsine ($tas=CH_3As\{(CH_2)_3As(CH_3)_2\}_2$) was seen as a route to achieving higher

coordination numbers with the tetrahalides of zirconium. This study led to the isolation of the compound $ZrBr_4$(tas) which was thought to contain a seven coordinate zirconium atom.[43] The higher coordination number of eight has received much attention and has been well reviewed.[44-46]. The eight coordinate 1:2 adducts $MX_4(diars)_2$ (M = Zr or Hf, X = Cl or Br)[47,48] are isomorphous with the corresponding titanium complex $TiCl_4(diars)_2$.[24] The analogous $ZrCl_4(dmpe)_2$ (dmpe = $Me_2PCH_2CH_2PMe_2$) complex has also been reported.[49] The reactions of zirconium and hafnium tetrahalides with an excess of dimethyl sulphoxide or a primary amide yield adducts of the type $MX_4(L)_n$ where n has values ranging from 2 to as high as 10. Several examples are listed below.

Complex	Ref
$ZrCl_4(DMSO)_n$ (n = 2, 3, 8, 9)	50-52
$HfCl_4(DMSO)_n$ (n = 2, 8, 9)	50-52
$MBr_4(DMSO)_n$ (n = 2, 10)	50, 51
$ZrCl_4(HCONH_2)_n$ (n = 4, 8, 10)	53

Although the compounds $MCl_4(DMSO)_8$[51] and $ZrCl_4(HCONH_2)_{10}$[53] appear to feature zirconium(IV) with extraordinarily high coordination numbers of 12 and 14 respectively, IR studies indicate the presence of both coordinated and non-coordinated ligands.

COORDINATION CHEMISTRY OF TIN TETRAHALIDES

Our interest lies in the coordination chemistry of tin tetrachloride, which often resembles that of $TiCl_4$. These tetrachlorides exists as monomers, containing four coordinate metal atoms in a tetrahedral geometry and are colourless distillable liquids, readily hydrolysed by water. Both are strong Lewis acids, reacting with a wide range of donor ligands such as, ethers and amines *etc,*.[54] For adducts of the type $SnX_4(L)_2$ (X=Cl, Br, I) the stereochemical placement of the ligands is frequently rationalised on steric grounds, whereby large ligands favour a *trans* placement thereby minimising steric interaction(s). Zahrobsky[55] has proposed a stereochemical model based on consideration of non-bonding interaction of ligands in $MX_4(L)_2$ systems in an attempt to predict stereochemical preference. This model suggests that all such systems should contain *cis* placed ligands regardless of the relative sizes of the donor atoms.

$SnX_4(L)_2$ Adducts

Considerable efforts have been directed at the study of six coordinate adducts of SnX_4. In many cases the question of preferred ligand placement has been answered by IR and/or NMR studies though not always unambiguously. Amongst those structurally characterised $SnCl_4(DMSO)_2$[56], $SnI_4(OPPh_3)_2$[57] and $SnCl_4(detu)_2$[58] (detu = 1,3 diethylthiourea) have a *cis* ligand placement. The latter compound is one of twenty-five *cis* octahedral adducts formed between SnX_4 and thiourea and urea in a study conducted by Calogero *et al.*[58] IR evidence suggests the thiourea ligand is S-bonded due to a positive shift of 34 cm^{-1} from the free detu ligand value for the ν(C-N) band at 1601 cm^{-1}; the far infrared region is indicative

of *cis* octahedral geometry. This is consistent with the trend seen in the other thiourea compounds which presumably contain S-bonded ligands.

Examples of *trans* octahedral geometry are provided by the adducts, $SnCl_4(PEt_3)_2$[59] and $SnCl_4(1,5\text{-DTCO})_2$[60], 1,5-DTCO=dithiacyclooctane. The latter compound is illustrated in Figure 5.

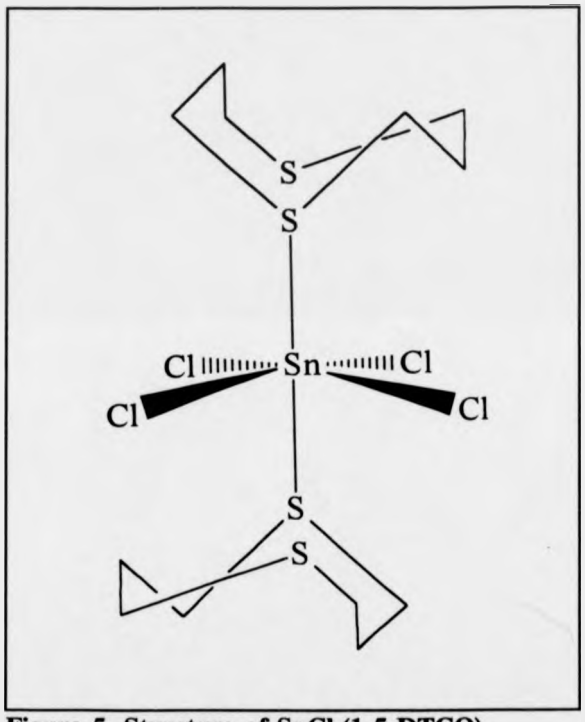


Figure 5. Structure of $SnCl_4(1,5\text{-DTCO})_2$

$SnX_4(B)$ Adducts (B=Bidentate Ligand)

Within this class the most abundant species are those containing O-donor ligands which is in keeping with the trend (O > N > S-donor) seen in other Sn(IV) and Ti(IV) compounds. Various N, N'-disubstituted dithiooxamide and oxamide ligands have been shown to form S, S' and O, O'-bidentate chelate complexes

with $SnBr_4$ in which the tin atoms are six coordinate with a distorted octahedral geometry.[61, 62]

All tin tetrahalides form 1:1 adducts with the bidentate N-donor ligand 2,2'bipyridyl yielding regular octahedral geometries.[63-65]

Coordination Numbers Other than Six

Compounds of the tin tetrahalides exhibiting a trigonal bipyramidal (tbp) coordination geometry are rare. Drager *et al*[66] have studied five coordinate Sn(IV) centres in heterocyclic ring systems. As a typical example, the compound $SnCl_2(SCH_2CH_2SCH_2CH_2S)$ features the metal in a pseudo tbp environment as illustrated in Figure 6.

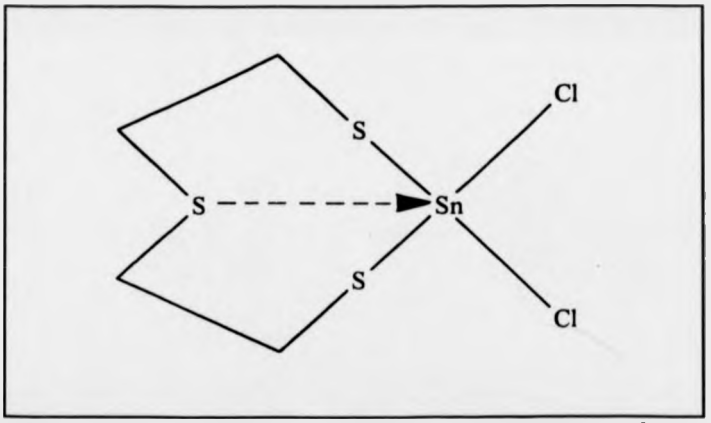


Figure 6. Schematic Representation of 2,2-dichloro-1,3,6,2-trithiastannoctane

A coordination number of seven is extremely rare in simple inorganic tin(IV) complexes. A search of the Daresbury Crystallographic database reveals only three examples.[67-69] However, the examples are not directly related to this study as they involve replacement of all or most of the halogen atoms with other donor atoms such as O, N, S and C.

The more contemporary example $SnMe_2Br_2 \cdot AZP$, (AZP=2,2'azopyridine) was isolated in 1990 by Rivarola *et al.*[69] This compound formed part of a systematic study aimed at isolating a series of adducts of Sn(IV) for subsequent X-ray study. Structural examination revealed a seven coordinate metal centre comprising, two methyl groups, three nitrogen atoms of the ligand and two bromine atoms. (Figure 7.)

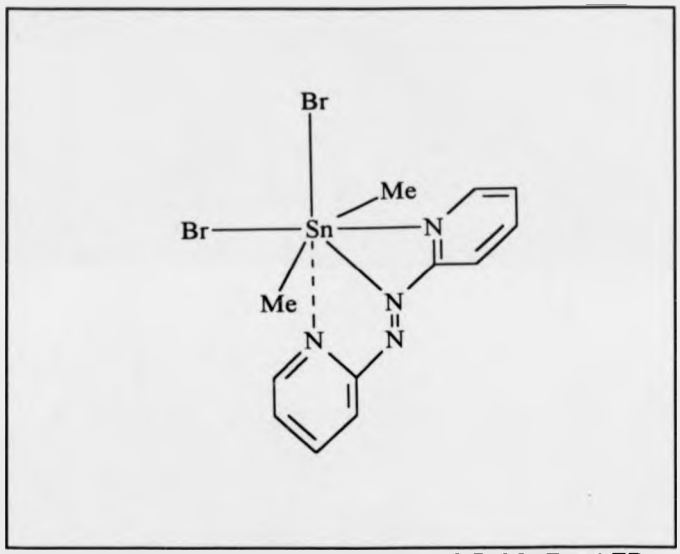


Figure 7. Schematic Representation of $SnMe_2Br_2 \cdot AZP$ (AZP=2,2'-Azopyridine)

CHAPTER TWO

HALIDE ABSTRACTION REACTIONS OF MCl_4

where M = Ti, Zr, Hf and Sn

HALIDE ABSTRACTION

INTRODUCTION

Chemistry of Antimony Pentachloride

Antimony pentachloride is a colourless liquid, requiring storage under an inert atmosphere. It is prepared by the action of chlorine gas on antimony trichloride.[7] The crystal structure (-30°C) consists of a trigonal bipyramidal monomer with bond lengths Sb-Cl (apical) 2.34 Å and Sb-Cl (equatorial) 2.29 Å.[70] These X-ray diffraction results correlate well with those obtained in the gas phase where the trigonal bipyramidal configuration is again adopted, with bond lengths 2.43 Å (apical) and 2.31 Å (equatorial).[71] Liquid phase Raman spectroscopic measurements also suggest a trigonal bipyramidal structure with the antimony atom somewhat displaced from the equatorial plane.[72]

Neutral Complex Formation

Molecular adduct formation occurs with oxygen, nitrogen and sulphur donors. For example, reaction of $SbCl_5$ with $(CH_3)_2SO$ yields a 1:1 addition compound, exhibiting a 6 coordinate Sb atom, to which dimethyl sulphoxide coordinates via the oxygen atom.[73]

In 1865 Weber[74] isolated the adduct $SbCl_5 \cdot SeOCl_2$, but X-ray characterisation was only achieved some 102 years later.[75] (Figure 8.)

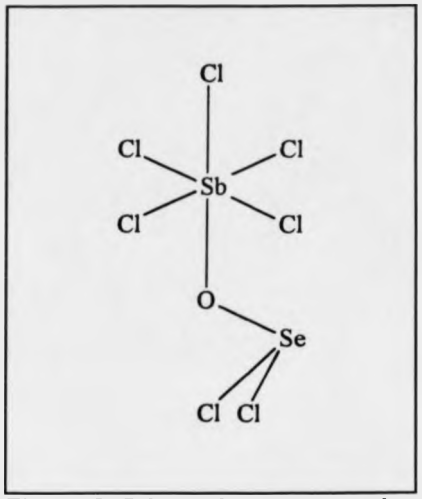


Figure 8. Schematic Representation of $SbCl_5 \cdot SeOCl_2$

This revealed a distorted octahedral geometry due to adjacent chlorine atoms bending towards the donor-acceptor bond. Reaction of S_4N_4 with 1 equivalent of $SbCl_5$ affords the expected molecular adduct $SbCl_5 \cdot S_4N_4$.[76] By contrast, reaction of S_4N_4 with an excess of $SbCl_5$ in liquid SO_2 results in a redox reaction yielding $(S_4N_4)(SbCl_6)_2$, consisting of non-interacting $(S_4N_4)^{2+}$ cations and $(SbCl_6)^-$ anions.[76] The reaction between $SbCl_5$ and ICl_3 produces an ionic solid in which the ions $(ICl_2)^+$ and $(SbCl_6)^-$ weakly interact forming chains.[77]

Organic Cations

The hexachloroantimonate anion has become a familiar anion in organic chemistry. The recurrent use of this anion arises because the salts general exhibit greater thermal stability in the crystalline state than the corresponding perchlorates or tetraphenylborates. They also display a higher solubility in a wider range of organic solvents. In many cases these organic hexachloroantimonate salts have

not arisen from direct halide abstraction but a pathway involving hydride exchange accompanied by redox.[78] (Eqn. 3)

$$R\text{-}H + 2SbCl_5 \rightarrow [R][SbCl_6] + SbCl_3 + HCl \qquad (3)$$

Direct halide abstraction is more common when phosphine groups or functional groups such as a carbonyl are present. The reaction of tertiary phosphines such as $PRCl_2$, PR_2Cl and PR_3 with excess $SbCl_5$ gives phosphonium and chlorophosphonium salts.[79] (Eqn. 4, 5)

$$PFCl_2 + SbCl_5 + Cl_2 \rightarrow [PFCl_3][SbCl_6] \qquad (4)$$

$$P(C_6H_5)_3Cl_2 + SbCl_5 \rightarrow [(C_6H_5)_3PCl][SbCl_6] \qquad (5)$$

The reactions with carbonyl containing reagents (eg RCOCl) are slightly more difficult to effect as they are dependant upon the type of R group present and the local conditions, (*eg*. nature of solvent). For example, halide abstraction is achieved if R is Me or Me_2CH, yielding $[RCO][SbCl_6]$ but when R is Et or Ph only simple molecular adducts are isolated. The solvent dependent nature of these reactions was demonstrated by Cheverier *et al.*[80] In this work the effect of two different solvents (CCl_4 and $CHCl_3$) on the reaction between *p*-toluoyl chloride and $SbCl_5$ was examined. The results are summarised in Equation 6.

$$Me(C_6H_4)COCl + SbCl_5 \xrightarrow{CCl_4} Me(C_6H_4)COCl \cdot SbCl_5 \qquad (6)$$

$$Me(C_6H_4)COCl + SbCl_5 \xrightarrow{CHCl_3} [Me(C_6H_4)CO][SbCl_6] \qquad (6)$$

Metal Cationic Species

Many of the early studies concerning halide abstraction from metal halides were conducted by Groeneveld and coworkers.[81-83] Groeneveld *et al* explored the action of $SbCl_5$ on systems containing mono, di and trivalent metal halides in the presence of the donor solvent MeCN, as indicated in Table 3.

Table 3. Metal Halides Studied by Groeneveld

MCl where M =	MCl_2 where M =	MCl_3 where M =
Li, Na, K, Rb, Cs, Cu, Ag, Au.[81]	Be, Mg, Ca, Sr, Ba, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pd, Hg.[82, 83]	Al, Ga, In, Cr, Cr, V, La.[83]

The primary concerns were stated as: (a) to determine the limit of chloride transfer and (b) to rationalise the changes seen in the infrared spectra of MeCN, upon coordination to the metal chloride.

The cationic species were formed as a result of complete chloride abstraction by the $SbCl_5$ from the metal chloride. In the case of mono valent systems formation of the cation is straightforward with respect to the number of possible products formed. (Eqn. 7)

$$MCl + SbCl_5 \rightarrow [M]^+[SbCl_6]^- \qquad (7)$$

(Solvent omitted for clarity)

On moving to the divalent systems, formation of both mono and divalent cations may be envisaged. (Eqns. 8, 9)

$$MCl_2 + SbCl_5 \rightarrow [MCl]^+ + [SbCl_6]^- \qquad (8)$$

$$MCl^+ + SbCl_5 \rightarrow [M]^{2+} + [SbCl_6]^- \qquad (9)$$

(Solvent omitted for clarity)

However, it soon became clear that mono cations (Eqn 8.) were not observed in such reactions. In order to pursue this further, Groeneveld extended the study to encompass trivalent metal halides. Here the problem becomes more intriguing, with the potential to form three cationic species *ie*. $[MCl_2]^+_{solv}$, $[MCl]^{2+}_{solv}$ or $[M]^{3+}_{solv}$. The results from this study are listed in Table 4. The products were characterised using microanalysis, conductometric titrations and infrared data. Of the twelve systems under consideration, half were found to allow removal of all three chlorides ions.

Table 4. Complex Formation between MCl_3 and $SbCl_5$ (taken from ref 83)

Transfer of 3 Cl^- ions	Transfer of 2 Cl^- ions	Transfer of 1 Cl^- ion	No Cl^- ion Transfer
$AlCl_3 \cdot 3SbCl_5 \cdot 9L$ $GaCl_3 \cdot 3SbCl_5 \cdot 9L$ $InCl_3 \cdot 3SbCl_5 \cdot 9L$ $CrCl_3 \cdot 3SbCl_5 \cdot 9L$ $LaCl_3 \cdot 3SbCl_5 \cdot 11L$ $VCl_3 \cdot 3SbCl_5 \cdot 9L$	$FeCl_3 \cdot 2SbCl_3 \cdot 5L$	$BCl_3 \cdot SbCl_5 \cdot 2L$ $TlCl_3 \cdot 2SbCl_5 \cdot 6L$ $BiCl_3 \cdot SbCl_5 \cdot 6L$	$AsCl_3$ $SbCl_3$

L = MeCN

Comparison of the latter two reactions ($AsCl_3$ and $SbCl_3$ with $SbCl_5$) with more recent reports may give some indication as to why halide abstraction did not occur in this instance. Firstly, evidence to support the existence of $SbCl_2^+$ is scant. One such reference is to the 1:1 adduct $SbCl_3 \cdot GaCl_3$ which consists of the ions $SbCl_2^+$ and $GaCl_4^-$.[84] The analogous reaction system SbF_3 with SbF_5 did not yield the expected simple adducts but complex polymeric cations $(Sb_6F_{13})^{5+}$ stabilised by the SbF_6^- anion.[85]

Inspection of the Daresbury Crystallographic Database reveals that citations of tin cations containing the fragment X-Sn-L (where X = F, Cl, Br or I and L = O, S or N) are meagre. It appears that the majority of these compounds arise from organotin derivatives complexed by multidentate ligands. Amongst the various types of organotin compounds, triorganotin complexes are of particular interest because of their biocidal activity. The earliest derivatives to be isolated had low aqueous solubility. This led to efforts to synthesise water soluble triorganotin biocides. Incorporating the Sn atom into either the cationic or anionic segment of salts of the type $[R_3SnL_2]^+X^-$ or $[R_3SnX_2]^- Y^+$ was identified as a possible route to increasing the aqueous solubility. It is the former cationic species which are of particular relevance to this discussion.[86] As a typical example we can cite [2,6-$(Me_2NCH_2)_2C_6H_3SnMe_2$][Br]. (Figure 9.)

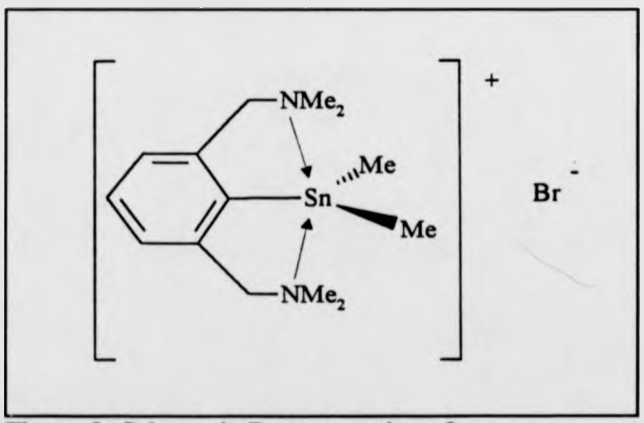


Figure 9. Schematic Representation of [2,6-$(Me_2NCH_2)_2C_6H_3SnMe_2$][Br]

The structural data reveals discrete monomeric triorganotin cations of $[(Me_2NCH_2)_2C_6H_3SnMe_2]^+$ in which the shortest Sn....Br distance is 4.99 Å. The

$Sn\text{-}C_3$ arrangement is almost planar with the two Me_2NCH_2 moieties occupying the axial positions in this trigonal bipyramidal structure. Previous to this work, Kumar Das[87] had studied organotin complexes with oxygen donor ligands. This was a fairly comprehensive study involving use of the halide abstracting agents $NaBPh_4$ and $KClO_4$ to generate Sn(IV) cations in the presence of the bidentate ligands: $Ph_2P(O)CH_2P(O)Ph_2$=(OPO), $Ph_2P(O)(CH_2)_2P(O)Ph_2$=(diphosO_2), $Ph_2As(O)CH_2As(O)Ph_2$=(OAsO) and the monodentate ligands Ph_3PO and Ph_3AsO. Numerous mono and dicationic species were isolated and characterised by NMR and IR spectroscopic measurements. Table 5.

Table 5. Mono and Dicationic Organotin Species

Ligand	Monocations	Dications
bipyO_2	$[Me_3SnL][BPh_4]$	$[Me_2SnL_2][BPh_4]_2$ $[Me_2SnL_2][PF_6]_2$ $[Me_2SnL_2][ClO_4]_2$
OPO	$[Me_3SnL][BPh_4]$ $[Ph_3SnL][BPh_4]$	$[Me_2SnL_2][BPh_4]$ $[Ph_2SnL_2][BPh_4]$
diphosO_2	$[Me_3SnL][BPh_4]$ $[Ph_3SnL][BPh_4]$	$[Me_2SnL_2][BPh_4]_2$ $[Ph_2SnL_2][BPh_4]_2$
OAsO	$[Me_3SnL][BPh_4]$	$[Me_2SnL_2][BPh_4]_2$
Ph_3PO	$[Me_3SnL][PF_6]$	$[Me_2SnL_4][PF_6]_2$ $[Me_2SnL_4][ClO_4]_2$
Ph_3AsO	$[Me_3SnL_2][PF_6]$	$[Me_2SnL_4][PF_6]_2$
HMPA	$[Me_3SnL_2][BPh_4]$ $[Ph_3SnL_2][BPh_4]$	$[Me_2SnL_4][BPh_4]_2$ $[Ph_2SnL_4][BPh_4]_2$
DMSO	$[Ph_3SnL_2][BPh_4]$	$[Ph_2SnL_4][BPh_4]_2$
DMF	$[Ph_3SnL_2][BPh_4]$	/

Reaction of 2, 2', 2''-terpyridyl with tin tetrachloride gave a compound formulated as $[Me_2SnCl(terpyridyl)][Me_2SnCl_3]$ on the basis of conductivity measurements.[88] Subsequent treatment with sodium tetraphenylborate gave $[Me_2SnCl(terpyridyl)][BPh_4]$. The possibility of two differing tin environments contained in the same complex made the former an attractive subject for crystallographic analysis, as such examples were rare at that time. (Figure 10)

This examination revealed that bonds to the tin atom in the cation departed from a regular octahedron in three ways:

1. N-Sn-N angles are less than 90°.
2. Cl displaced towards ring C of the terpyridyl group, while both methyl groups are displaced towards A.
3. The methyl groups bend away from terpyridyl group.

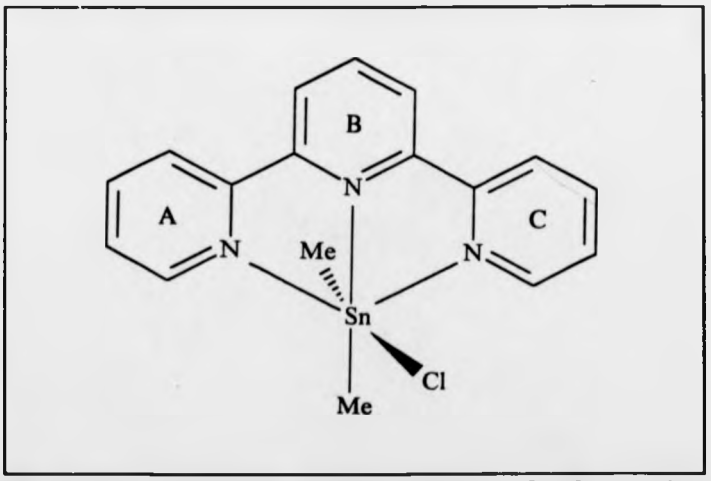


Figure 10. Schematic Representation of the cation $[Me_2SnCl(terpyridyl)]^+$

Of particular interest with regard to our studies of Group 4 transition metals, Groeneveld *et al*[83] reported that $TiCl_4$ and $SbCl_5$ in acetonitrile do not react to yield a cationic species. Gutmann and Himmel[89] have studied the reactions of $TiCl_4$ and $ZrCl_4$ with $SbCl_5$ in the solvent $POCl_3$. (Eqn 10)

$$MCl_4 + SbCl_5 \rightarrow [MCl_3(POCl_3)_3][SbCl_6] \qquad (10)$$

M = Ti, Zr L = $POCl_3$

The resulting products were formulated as antimonate(V) salts based on analytical data. An independent investigation of this system undertaken by Adolfson *et al*,[90] resulted in the same compounds being isolating and characterised using microanalytical data and conductance measurements.

Alternative Halide Abstracting Agents

The reagent $SbCl_5$ can be successfully replaced by other halide abstracting agents such as $FeCl_3$, $SnCl_2$ or $ZnCl_2$. Although the reaction system $FeCl_3/SbCl_5$[91] yields a $FeCl_2^+$ cation, $FeCl_3$ has a quite considerable chloride abstracting ability itself as shown in the reactions $FeCl_3/PCl_5$[92] and $FeCl_3/MgCl_2$[93] . Similarly, Gutmann *et al*[94] utilised the halide abstracting ability of $FeCl_3$ with $TiCl_4$ to produce $[TiCl_3(POCl_3)_3][FeCl_4]$. Studies of the $TiCl_4/POCl_3$ system with various halide abstracting agents continued, leading to a proposal that several titanium species existed in solution depending on the halide abstracting agent present.[95] Sobota[96] has demonstrated the usefulness of $SnCl_2$ as a halide abstracting agent. Direct reaction between $[TiCl_4(THF)_2]$ and $SnCl_2$ in THF yields the paramagnetic salt [*trans*-$TiCl_2(THF)_4$][$SnCl_5(THF)$]. This complex was also isolated from a reaction

between $[TiCl_3(THF)_3]$ and $SnCl_4$ in the same solvent.[96] Halide abstraction by $ZnCl_2$ effects Cl^- ion removal from $TiCl_3$ in THF providing a convenient route to $[TiCl_2(THF)_4][ZnCl_3(THF)]$ without redox interference.[97] The action of but-2-yne or hexamethylbenzene on solutions of $TiCl_4$ provides the cation $[\{\eta^6\text{-}C_6Me_6 TiCl_3\}]^+$.[98] (Figure 11.)

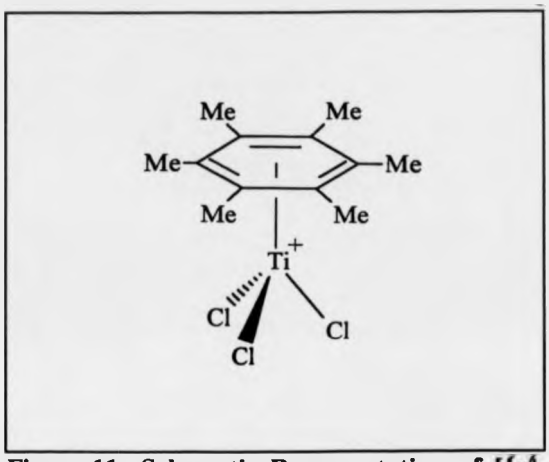


Figure 11. Schematic Representation of $[\{\eta^6\text{-}C_6Me_6TiCl_3][Ti_2Cl_9]$

Role of the Solvent

Complex formation and subsequent complex stability may be effected by the nature of the reaction medium. Several studies have investigated the role the solvent plays in these processes. Russian chemists[99] explored the use of esters as solvent/ligand *eg*. $TiCl_4$ and $InBr_3$ produce the salt $[TiCl_3L_3][InBr_3Cl]$ (where L = $C_3H_7CO_2C_2H_5$). Other solvents which have been used to this effect include pyridine and nitromethane. However, there is an incipient problem associated with the $SbCl_6^-$ anion, *viz* the known oxidising potential of Sb(V). For example, (a) the $SbCl_6^-$ anion is known to polymerise THF,[100] as well as other cyclic ethers

such as styrene oxide[101] and (b) the 2, 4, 6-tri-t-butyl phenoxide ion was oxidised to 2, 4, 6-tri-t-butyl phenoxide radical by tropylium hexachloroantimonate but not by the corresponding tetrafluoroborate or perchlorate.[102]

Fortunately with careful choice of solvent this oxidising potential of antimony pentachloride is not always detrimental. Several transition metal compounds have been prepared via redox reactions of $SbCl_5$.[103] (Eqn. 11, 12)

$$W(CO)_3triars + 2SbCl_5 \rightarrow [W(CO)_3triarsCl][SbCl_6] + SbCl_3 \quad (11)$$

$$W(CO)_3hmb + 2\ SbCl_5 \rightarrow [W(CO)_3hmbCl][SbCl_6] + SbCl_3 \quad (12)$$

Cp and Cp* Group 4 Cationic Species

The ligands cyclopentadienyl (Cp) and pentamethylcyclopentadienyl (Cp^*) are bulky six electron donor ligands forming strong bonds with the electron deficient elements of Group 4. Those species with substituted Cp groups often have an enhanced thermal and hydrolytic stability owing to the shielding effect of these large groups. In addition, complexes containing the pentamethylcyclopentadienyl group (Cp^*) usually exhibit a greater solubility than those involving the simple Cp ligand.

Several synthetic strategies have been investigated in the search for cationic Group 4 metal species containing Cp and Cp^* groups. These routes include a) halide abstraction, b) oxidation of M(III) and c) alkane elimination.

a) Halide Abstraction

In a search for potential antitumour agents, Thewalt *et al*[104] were first to demonstrate the ability of metal halides to remove Cl^- ions from Cp_2TiCl_2. They successfully isolated and characterised $[Cp_2TiCl(MeCN)][FeCl_4]$ from the action of $FeCl_3$ upon Cp_2TiCl_2 in MeCN. Thewalt and Honold[105] examined the possibility of removing chloride ions from $Cp^*_2TiCl_2$ with $AgCF_3SO_3$ in THF containing a trace of water. Two compounds, $[Cp^*_2Ti(OH)(H_2O)][CF_3SO_3]$, $[Cp^*_2Ti(OH)_2][CF_3SO_3]_2$ and an oxo bridged species were successfully isolated. Other useful counter anions include; ClO_4^-, BF_4^-, BPh_4^- and PF_6^-. White[106] demonstrated this in his work with Cp_2TiCl_2 and several silver salts (AgX where X = ClO_4, BF_4, BPh_4, PF_6) in ethyl-3-ketobutyrate ($C_6H_9O_3$), which resulted in the isolation of $[Cp_2Ti(C_6H_9O_3)][X]$. Similarly, $Tl(PF_6)$ will react with Cp_2TiI_2 in acetonitrile to produce the dicationic complex $[Cp_2Ti(MeCN)_2][PF_6]_2$.[107] However such anionic salts cannot be used with impunity. Bochmann and Wilson[108] in their studies of the synthesis and insertion reactions of cationic alkylbis(cyclopentadienyl)titanium complexes encountered problems. In the presence of base, facile F^- abstraction occurred from these anions, *eg.* $[Cp_2TiMe_2][BF_4]$ yeilded $Cp_2Ti(Me)F$ and Cp_2TiF_2. This necessitated the use of the BPh_4^- salt, as shown below. (Eqn. 13.)

$$[Cp_2TiMe(NH_3)][BPh_4] \rightarrow [Cp_2TiMe(MeCN)][BPh_4] \quad (13)$$

Rather than allowing solvent molecules to coordinatively saturate the metal centre, ligands such as acac,[109] (acac=acetylacetonate anion) have been used. This strategy allows the incoming ligand to displace a Cl^- ion which then acts as the counter anion.

Alternatively the Cl^- ion may be incorporated in the metal coordination sphere forming a new anion.[109] (Eqn 14)

$$[Cp_2Ti(L)Cl] + MX_3 \rightarrow [Cp_2Ti(L)][M(Cl)X_3] \quad (14)$$

M = Ga, In, Tl L = acetylacetonate anion, (acac),

X = Cl, Br, I

b) Oxidation of M(III)

The one electron oxidation of M(III) complexes (M=Ti, Zr or Hf) by Ag(I) or Tl(I) salts provides a suitable route to cationic coordinatively unsaturated organometallic compounds. Royo and Cuenca[110] were among the first to isolate cationic species using this method *eg.* oxidation of $[Cp_2M(\mu\text{-}Cl)]_2$ with either $AgBF_4$ or $TlBF_4$. (Eqn. 15)

$$[Cp_2M(\mu\text{-}Cl)]_2 + 2AgBF_4 \rightarrow [Cp_2M(\mu\text{-}Cl)]_2[BF_4]_2 + 2Ag^\circ \quad (15)$$

M=Zr, Hf

The subsequent reaction with monodentate ligands affords $[Cp_2MClL]^+$ (L=$OPPh_3$ or $NHPh_2$) or dinuclear cationic derivatives $[(Cp_2MCl)_2(\mu\text{-}L')]^{2+}$ with bidentate ligands (L' = bipy or dppe).[110]

This route was studied extensively by Bochmann *et al*[111] who synthesised a number of compounds with a variety of different ligands, an example of which includes $[Cp^*_2TiMe(THF)][BPh_4]$. This was prepared by the action of $AgBPh_4$ on Cp^*_2TiMe in THF. (Eqn. 16)

$$Cp^*_2TiMe + AgBPh_4 \rightarrow [Cp^*_2TiMe(THF)][BPh_4] + Ag^\circ \quad (16)$$

c) Alkane Elimination

Bochmann and Lancaster[112] made use of alkane elimination to isolate new cationic compounds containing the 14 electron cation $[Cp_2TiMe]^+$. (Eqn. 17)

$$Cp_2TiMe_2 + [HNEt_2Ph][BPh_4] \rightarrow$$

$$[Cp_2TiMe][BPh_4] + CH_4 + PhNEt_2 \qquad (17)$$

The use of the bulky $[HNEt_2Ph]^+$ was a key point in the development of this work as its low basicity allows the production of a coordinatively unsaturated metal centre. Such cationic species are thought to be the active agent in homogeneous Ziegler-Natta catalysis. A discussion covering Ziegler-Natta catalysis is beyond the scope of this thesis but an excellent review, by Jordan,[113] is available.

RESULTS AND DISCUSSION

Having recognised the potent halide abstracting ability of $SbCl_5$ we set out to isolate and characterise the mono, di and tricationic species (assumed to be six coordinated) listed below from their respective metal halides. (Eqn. 18)

$$MCl_4 + SbCl_5 \rightarrow [MCl_3L_3][SbCl_6]$$

$$\downarrow SbCl_5$$

$$MCl_4 + 2SbCl_5 \rightarrow [MCl_2L_4][SbCl_6]_2 \qquad (18)$$

$$\downarrow SbCl_5$$

$$MCl_4 + 3SbCl_5 \rightarrow [MClL_5][SbCl]_3$$

where M = Ti, Zr, Hf, Sn. and L = MeCN

The titanium cation $[TiCl_3(MeCN)_3][SbCl_6]$ which was isolated by previous workers in this laboratories[91] will be discussed later, in relation to the results obtained from this study.

Treatment of the metal halides with increased stoichiometric ratios of $SbCl_5$ has provided the species $[MCl_{4-n}]^{n+}$ where M = Ti, n=1 or 3, recrystallised from MeCN and M=Sn, Zr and Hf, n=1. In the latter two (Zr, Hf) cases the compounds were recrystallised from 1,4-dioxane owing to their extremely high solubility in MeCN.

The presence of the hexachloroantimonate anion $[SbCl_6]^-$ can be monitored using infrared and UV-VIS spectroscopy in conjunction with microanalytical data.

In the far infrared region (450 - 200 cm^{-1}), the presence of the $[SbCl_6]^-$ anion is established by a very intense, symmetrical band at approximately 345 cm^{-1}. This is attributed to the very strong Sb-Cl ν_3 mode $[F_{1u}]$ observed at 346 cm^{-1} for the complex $[K][SbCl_6]$.[114] This compares with the intense band at 348 cm^{-1} in the IR spectrum of $[pyH][SbCl_6]$[115]. However, if the compound retains a M-Cl bond this band may incorporate some coupling between ν(Sb-Cl) and ν(M-Cl).

The $[SbCl_6]^-$ ion also has a distinctive charge transfer band in its electronic spectrum. This appears at 272 nm in acetonitrile solution.[116]

Each of the cationic species under investigation, incorporating MeCN ligands, exhibits a doublet in the 2330-2280 cm^{-1} region of the infrared spectra. This is characteristic of ν(CN) for coordinated acetonitrile when compared with bands at 2293 and 2255 cm^{-1} for the free ligand. The magnitude of this shift +(35-50) cm^{-1} implies MeCN forms a strong coordinate bond to the metal centre.

In contrast, those complexes incorporating a 1,4-dioxane ligand in their coordination sphere exhibit a low energy shift of the ν(C-O-C) stretching band. Typically this shift is of -(15-17) cm^{-1} with respect to the ν(C-O-C) band of the free ligand (1125 cm^{-1}).

Removal of One Chloride Ion

Reaction of $SnCl_4$ with 1 Equivalent of $SbCl_5$

The reaction of tin tetrachloride with 1 equivalent of $SbCl_5$ in acetonitrile yields a buff coloured solid. Following recrystallisation the product was deposited as small cubic crystals. Efforts to encapsulate them in capillary tubes were unsuccessful. On the basis of microanalytical data the product can be formulated as $SnCl_4 \cdot SbCl_5 \cdot 3MeCN$. This was interpreted as the formation of the

hexachloroantimonate salt $[SnCl_3(MeCN)_3][SbCl_6]$ following IR and UV spectroscopic measurements. Bands in the IR spectrum characteristic of coordinated MeCN were observed at 2332 and 2295 cm^{-1}, with an intense band in the UV spectrum at 37,051 cm^{-1} indicating the presence of $SbCl_6^-$.

In the absence of structural data comparison of the tin cation with the analogous structurally characterised *fac*-$[TiCl_3(MeCN)_3][SbCl_6]$[91] implies a similar *fac* arrangement of ligands. The compound can be considered as MX_3L_3, the *fac* isomer of which belongs to the point group C_{3v} and is expected to give two IR active bands whilst the *mer* isomer has three IR active bands (C_{2v}). However, this direct analysis merits some caution due to the presence of the strong Sb-Cl stretching band (345 cm^{-1}) and the medium band at 380 cm^{-1} assigned to the δ(CCN) bending mode of the (solvent) acetonitrile. For example the adduct $SnCl_4(MeCN)_2$ has a weak band at approximately 420 cm^{-1} due to coordinated acetonitrile and a much more intense band from Sn-Cl stretching at 333-345 cm^{-1}.[117] A weak δ(CCN) band occurs at 410 cm^{-1} in the adduct $SbCl_5 \cdot MeCN$.[115]

Cationic Species Of Zirconium and Hafnium

The reactions were carried out using 1:1 stoichiometry with an excess of acetonitrile. (Eqn 19)

$$MCl_4 + SbCl_5 \rightarrow [MCl_3L_x][SbCl_6] \qquad (19)$$

L = MeCN, M = Zr, x=4 and Hf, x = 5

The resulting products were recrystallised from 1,4-dioxane, as the products could not be recovered in a crystalline state from MeCN. The microanalytical data for these compounds which is reported in Table 6 suggests the products have the

empirical formulation $ZrCl_4 \cdot SbCl_5 \cdot 4$(1,4-dioxane) and $HfCl_4 \cdot SbCl_5 \cdot 5$(1,4-dioxane).

Table 6. Microanalytical Data for Zirconium and Hafnium Monocations

Compound	Analytical Data calc/obs (%) C	H	Cl
$ZrCl_4 \cdot SbCl_5 \cdot 4$(1,4-dioxane)	21.73, 21.96,	3.65, 4.00,	36.08 36.19
$HfCl_4 \cdot SbCl_5 \cdot 5$(1,4-dioxane)	22.65, 22.80,	3.80, 4.37,	30.11 30.97

This was interpreted as the formation of hexachloroantimonate species $[MCl_3L_x][SbCl_6]$ as IR bands characteristic of $SbCl_6^-$ are seen at 345 cm^{-1}. In addition bands corresponding to 1,4-dioxane, ν(C-O-C), shift to lower wavenumbers (1108 cm^{-1} for Zr and 1110 cm^{-1} for Hf), with respect to the free ligand 1125 cm^{-1}. IR data for the initial and recrystallised products is given in Table 7.

Table 7. Spectroscopic Data for Selected Compounds Containing Donor Ligands

Compound	ν(C-O-C) cm^{-1} L=1,4-dioxane	ν(CN) cm^{-1} L=MeCN
1,4-dioxane	1125	-
MeCN	-	2293, 2255
$[ZrCl_3L_4][SbCl_6]$	1108	2315, 2288
$[HfCl_3L_5][SbCl_6]$	1110	2318, 2290

In comparison with their titanium and tin counterparts the microanalytical data may be interpreted as an increase in coordination number of the metal centre or that 1,4-dioxane molecules are 'trapped' as lattice solvate. Following consideration of the above evidence, several formulations are possible for the compounds:

1.	$[MCl_3L_3][SbCl_6]\cdot 2L$	M = Zr or Hf
2.	$[MCl_3L_4][SbCl_6]\cdot L$	L = 1, 4-dioxane
3.	$[MCl_3L_5][SbCl_6]$	

On the basis of the available spectroscopic evidence it is difficult to say which is the most likely formulation.

However, Troyanov *et al*[118/119] studied analogous $ZrBr_4$ and ZrI_4 systems isolating compounds of composition $2ZrBr_4\cdot 5MeCN$ and $2ZrI_4\cdot 5MeCN$. Structural characterisation revealed the compounds exist as discrete cations and anions of the form, $[ZrBr_3(MeCN)_4][ZrBr_5(MeCN)]$ and $[ZrI_3(MeCN)_4][ZrI_5(MeCN)]\cdot MeCN$. In each cation the metal atom is seven coordinate and is formed as a result of halide transfer to another zirconium tetrahalide. In light of this evidence it is possible to suggest the cation derived from $ZrCl_4$ in our study may favour a similar formulation, that of $[ZrCl_3(C_4H_8O_2)_4][SbCl_6]$. The similar ionic radii of zirconium and hafnium (1.44/1.45 Å for (0) and 0.87/0.88 Å for (+4)) may permit an analogous situation but with a molecule of dioxane encapsulated in the lattice of the compound, $[HfCl_3(C_4H_8O_2)_4][SbCl_6]\cdot C_4H_8O_2$.

Reaction of $TiCl_3(MeCN)_3$ with $SbCl_5$

Treatment of the adduct $TiCl_3(MeCN)_3$ with $SbCl_5$ provides a yellow product which was not the expected species, $[TiCl_2(MeCN)_4][SbCl_6]$. The yellow solid was characterised as the adduct $TiCl_4(MeCN)_2$, serving to demonstrate the oxidising ability of $SbCl_5$. The reduction product was not pursued.

In an attempt to remove this inherent redox problem the halide abstracting agent $NaBPh_4$ was employed. This approach met with little success, yielding starting reagents apparently unchanged. The preparation of Ti(III) cationic species is generally a facile process. An example of such a species can be seen in $Cs_2[TiCl_2(H_2O)]Cl_3$ which contains the cation *trans*-$[TiCl_2(H_2O)_4]^+$. This was prepared by dissolving stoichiometric amounts of $TiCl_3$ and CsCl in a minimum amount of 2M HCl.[120] A further example has been reported by Caulton *et al.*[97] The compound [*trans*-$TiCl_2(THF)_4$][$ZnCl_3(THF)$] was isolated following halide abstraction from $TiCl_3$ by $ZnCl_2$.[97]

Removal of Two Chloride Ions

In an effort to obtain the dicationic species $[MCl_2L_4][SbCl_6]_2$ two complementary approaches were used, *ie.* direct and sequential halide abstraction: (Eqn. 20 and 21)

$$1.\quad MCl_4 + 2\,SbCl_5 \rightarrow [MCl_2L_4][SbCl_6]_2 \qquad (20)$$

$$2.\quad [MCl_3L_3][SbCl_6] + SbCl_5 \rightarrow [MCl_2L_4][SbCl_6]_2 \qquad (21)$$

In the case of titanium, each method gave two products, a yellow powder and a small quantity of emerald green crystals.

Characterisation of the yellow powder revealed the previously isolated $[TiCl_3(MeCN)_3][SbCl_6]$. Microanalytical data for the crystalline product suggests this has the formulation $TiCl_4 \cdot 3SbCl_5 \cdot 7MeCN$ which can be interpreted as the tricationic species, $[TiClL_5][SbCl_6]_3 \cdot 2L$. The formation of such a species was thought to arise from the desired dicationic species which has subsequently redistributed to yield both a monocation and a trication. (Eqn. 22)

$$2[TiCl_2L_4][SbCl_6]_2 \rightarrow [TiCl_3L_3][SbCl_6] + [TiClL_5][SbCl_6]_3 \quad (22)$$

Similar reactions with MCl_4 (M=Sn, Zr and Hf) gave oily products which were extremely sensitive to air/moisture hydrolysis. All the products deteriorated rapidly and the reactions were not pursued.

Removal of Three Chloride Ions

Generation of the salt $[TiClL_5][SbCl_6]_3$ has been effected by reacting $TiCl_4$ with a healthy excess of $SbCl_5$. The emerald green crystals which deposit from the reaction of $TiCl_4$ following recrystallisation from $MeCN/CH_2Cl_2$ are extremely sensitive to air/moisture, rapidly deteriorating when removed from the mother liquors. (Microanalytical and spectroscopic data is listed in Table 42.) Suitable crystals were eventually mounted in glass capillary tubes and examined by X-ray diffraction methods. Following data collection, complete structural elucidation was not achieved. Preliminary details reveal the crystal is of the orthorhombic type with a = 11.921, b = 24.004 and c = 20.616 Å. These initial findings point towards a complex of composition $[TiClL_7][SbCl_6]_3$. Three discrete $SbCl_6^-$ anions are observed per titanium atom which is eight coordinate. This is a unique structural arrangement for titanium. Previously, titanium has only enjoyed a

coordination number of eight with multidentate ligands, namely the bidentate ligand *o*-phenyl bis (dimethylarsine), as witnessed in the compound $TiCl_4(diars)_2$.[24] It is important to note that an excess of $SbCl_5$ ($TiCl_4$: $SbCl_5$, 1:5) is essential for the removal of three chloride ions from $TiCl_4$. A recent publication notes that complete chloride abstraction from $CpTiCl_3$ can only be achieved using an excess of $SbCl_5$ ($CpTiCl_3$:$SbCl_5$, 1:6).[121]

The halides MCl_4 (M=Zr, Hf and Sn) were also reacted with an excess of $SbCl_5$. Following recrystallisation, from MeCN, the products were obtained as finely divided powders. The products were extremely sensitive to air/moisture hydrolysis, deteriorating rapidly and were not pursued.

Variation in Ti-Cl Bond Distances

On moving from anionic chloro-titanium compounds through neutral to cationic species we can reasonably expect to see a distinct variation in the Ti-Cl bond length. The data for several pertinent octahedral examples is displayed in Table 8 and as a plot of Ti-Cl bond length *vs* charge in Figure 12.

Table 8. Bond Lengths of Selected Octahedral Chloro-Titanium Compounds

Species	$[TiCl_6]^{2-}$	$^{*}[TiCl_5L]^{-}$	$TiCl_4(MeCN)_2$	$[TiCl_3L_3]^{+}$
Charge	2^{-}	1^{-}	0	1^{+}
Averaged d(Ti-Cl) Å	2.339	2.296	2.240	2.186
Ref	122	123	124	91

*The acetonitrile ligand was used in all compounds with the exception of $[TiClL_5]^{-}$ which incorporates the THF ligand.

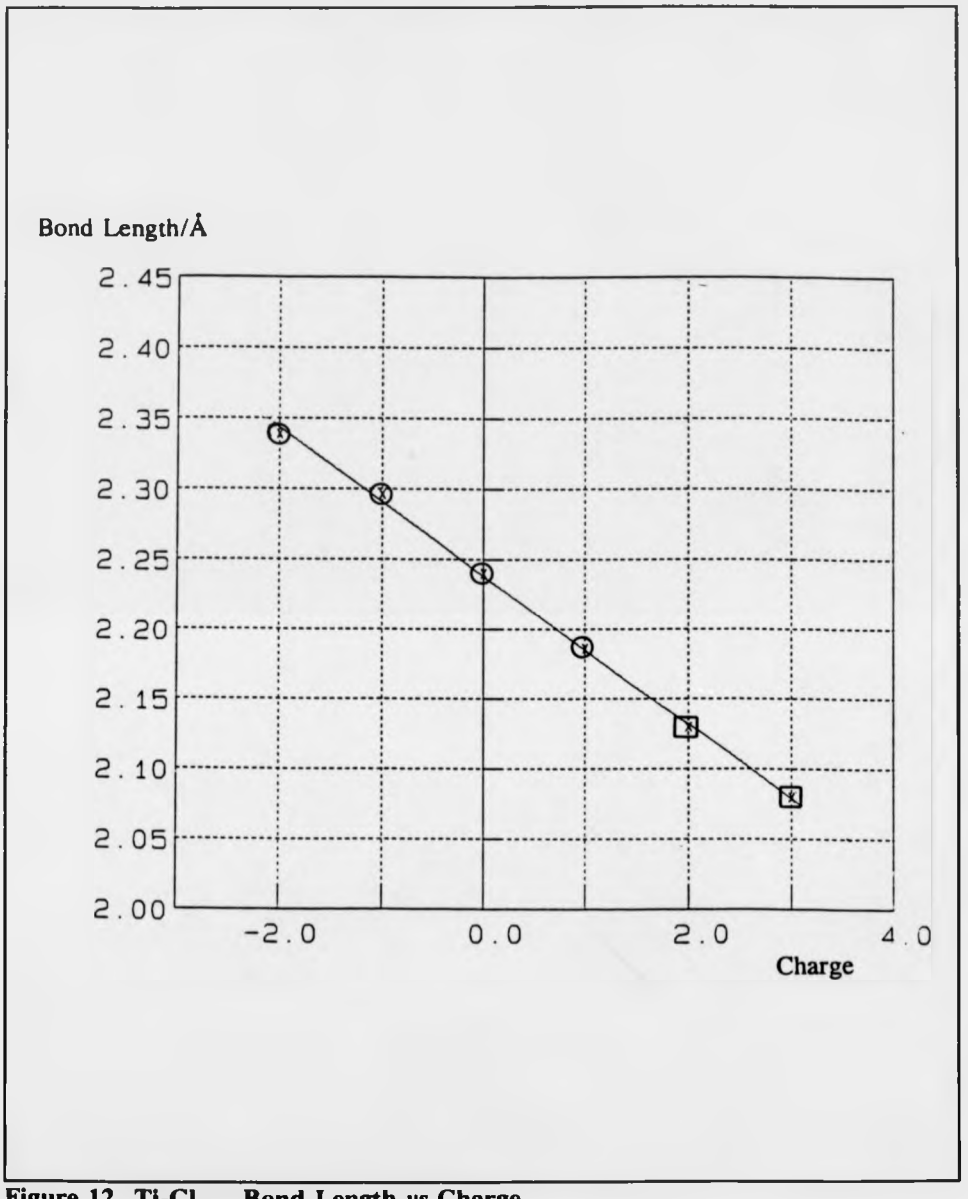


Figure 12. Ti-Cl$_{(Oh)}$ Bond Length *vs* Charge

Averaged Literature Value ○

Extrapolated Value □

The Ti-Cl bond length in the cation $[TiCl_3L_3]^+$ (2.18 Å) is little changed from that of the neutral octahedral adduct $TiCl_4(MeCN)_2$ (2.24 Å). In order to maintain the stability of the higher charged cations, it might be expected that the remaining chloride ions are held more tightly, thus reducing the bond length whilst the vacant coordination sites are saturated with solvent molecules. This is evident from the slightly greater reduction in the bond length (extrapolated) for both the dication (2.13 Å) and the trication (2.08 Å) in comparison with the monocation and neutral adduct. Such a contraction in the bond length is to be expected as removal of a chloride ion(s) reduces the electron density at the metal centre and hence increases the charge/radius ratio. (Table 9)

Crystallographic data is not available to compare with these extrapolated values.

Table 9. Correlation of Extrapolated Titanium Cation Bond Length with Charge/Radius Ratio

Species[a]	Charge	Ionic Radius[125] (Å)	Charge/Radius Ratio	Bond Length (Å)
$TiCl_3^+$	1+	0.96	1.04	2.18*
$TiCl_2^{2+}$	2+	0.94	2.13	2.13
$TiCl^{3+}$	3+	0.76	3.95	2.08

a The MeCN ligands omitted for clarity.
* This bond length is taken from the structurally characterised $[TiCl_3(MeCN)_3][SbCl_6]$[91]

Similarly, loss of electron density is consistent with the reduction (0.043 Å) in bond length seen on moving from the doubly charged anion $[TiCl_6]^{2-}$ (2.339 Å) to the anion $[TiCl_5(THF)]^-$ (2.296 Å).

Mechanism of Halide Transfer Using Antimony Pentachloride

Although the halide transfer mechanism is yet to be unequivocally resolved, it is possible to speculate upon a pathway. One possible route to accomplishing halide transfer is via a halogen bridged intermediate. (Figure 13)

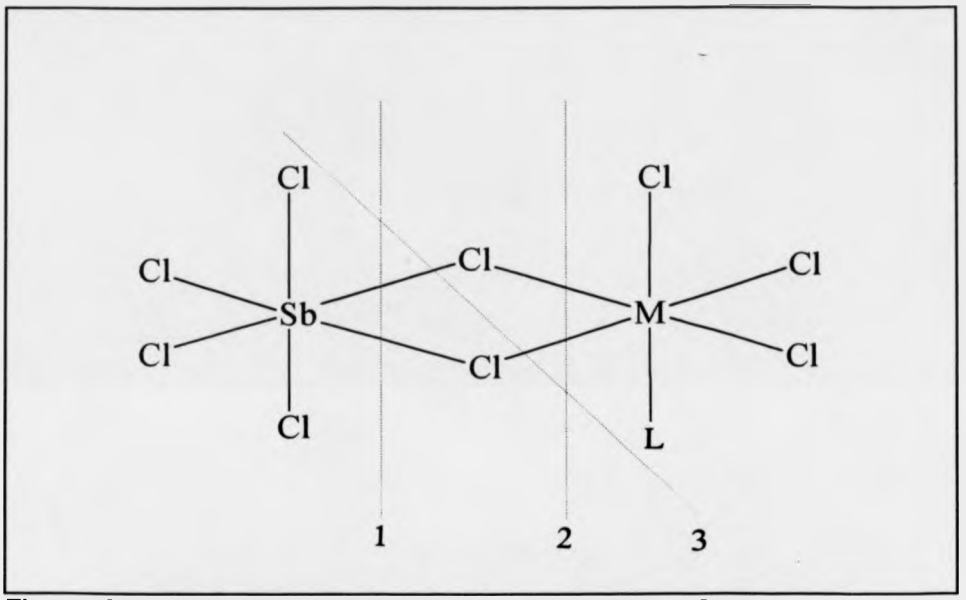


Figure 13. Proposed Bridged Intermediate in Halide Transfer

Halide transfer with bond cleavage at 2 is most desirable affording the required transition metal cation. Regeneration of the starting materials is envisaged through cleavage at 3. Cleavage along (1) implicates MCl_4 as the halogen acceptor yielding MCl_5^- which is feasible, but with the proviso that Sb(V) will relinquish a chloride ion offering a route to the cation $SbCl_4^+$. This route is somewhat unfavourable as it requires M(IV) to be a stronger halide acceptor than the Sb(V).

Although, the halide bridged species envisaged above have evaded isolation, Lorcher *et al*[126] isolated the bridged compound $Cl_3VNCl(SbCl_5)_2$ from the reaction system $Cl_3VNCl/SbCl_5$. This is the only example where a halogen bridged unit has been structurally characterised. The product consists of two $SbCl_5$ units halogen bridged by Cl_3VNCl leading to greatly distorted octahedral geometries around the vanadium and each antimony. (Figure 14)

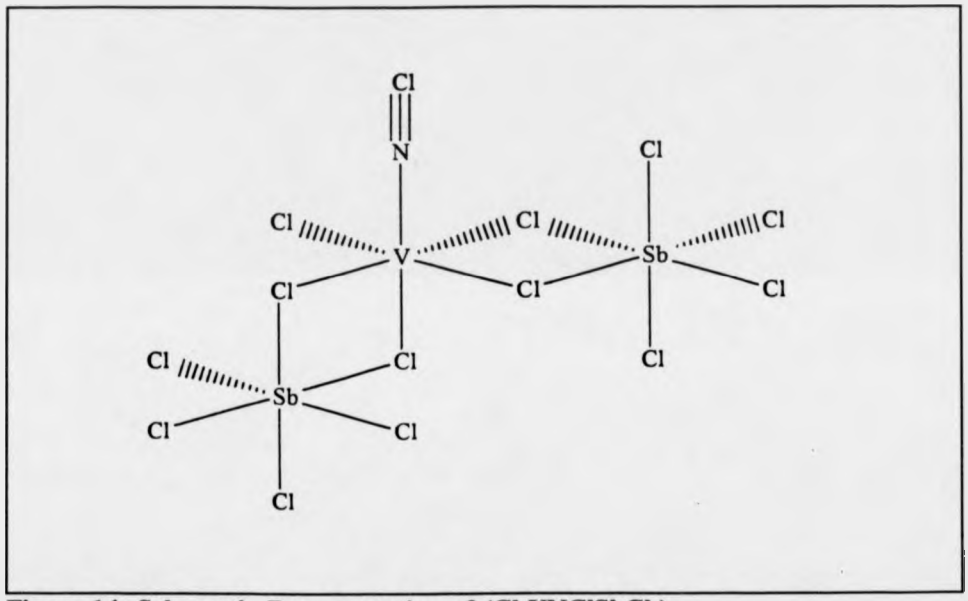


Figure 14. Schematic Representation of $(Cl_3VNClSbCl_5)_2$

Comparison of IR Data for the Cationic Species Containing MeCN Ligands

Upon coordination, the ν(CN) bands in each of the cations displays the familiar high energy shift. Table 10 lists the position of the bands and the extent of the shifts.

Table 10. IR Data for ν(CN) Bands in Compounds with MeCN Ligands

Species	ν(CN) cm^{-1}	$\Delta\nu$(CN) cm^{-1}
MeCN	2293, 2255	-
$TiCl_4(MeCN)_2$	2310, 2303, 2282, 2275	17, 10, 27, 20
$ZrCl_4(MeCN)_2$	2310, 2279	17, 24
$HfCl_4(MeCN)_2$	2311, 2282	18, 27
$SnCl_4(MeCN)_2$	2312, 2280	19, 25
$[TiCl_3L_3][SbCl_6]$	2322, 2299	29, 44
$[ZrCl_3L_3][SbCl_6]$	2310, 2285	17, 30
$[HfCl_3L_3][SbCl_6]$	2315, 2290	22, 35
$[SnCl_3L_3][SbCl_6]$	2322, 2295	29, 40
$[TiCl_3L_3][BPh_4]$	2321, 2298	28, 43
$[TiCl_3L_3][BF_4]$	2322, 2298	29, 43
$[TiClL_5][SbCl_6]_3$	2322, 2298	29, 43

Summary and Conclusions

This work clearly demonstrates that the use of antimony pentachloride offers a convenient route to Group 4 cationic species which often display a greater thermal stability than their tetraphenylborate counterparts.

The following cationic species have been isolated and characterised using spectroscopic and microanalytical measurements:

$[SnCl_3(1,4\text{-dioxane})_3][SbCl_6]$	CN = 6
$[ZrCl_3(1,4\text{-dioxane})_4][SbCl_6]$	CN = 7
$[HfCl_3(1,4\text{-dioxane})_4][SbCl_6]\cdot 1,4\text{-dioxane}$	CN = 7
$[TiCl(MeCN)_7][SbCl_6]_3$	CN = 8
$[TiCl_3(MeCN)_3][BPh_4]$	CN = 6
$[TiCl_3(MeCN)_3][BF_4]$	CN = 6

It appears both titanium and tin favour six coordination in the species $[MCl_3L_3][SbCl_6]$ whilst, deviations from this are observed for the larger zirconium and hafnium, which adopt a coordination number of seven.

The greatly increased positive charge on the titanium centre in $[TiClL_7][SbCl_6]_3$ not only facilitates an increasing number of coordinated ligands but also (presumably) a tighter hold on the remaining chlorine atom in an effort to maximise its π-donating interaction. As yet structural evidence to confirm a much shorter (expected) M-Cl bond length is not available. This species appears to represent the limit of halide abstraction.

CHAPTER THREE

CROWN ETHERS

CROWN ETHERS

INTRODUCTION

The isolation of dibenzo-18-crown-6 by Pedersen in 1967[127] and his subsequent observation that this ligand displayed a selectivity for alkali cations was a landmark. This heralded a major impetus in the synthesis and investigation of their remarkable properties. Since the discovery by Pedersen an overwhelming number of synthetic macrocycles have been isolated, fuelling interest in all aspects of their chemistry. The creation of a new substance often leads to a search for possible applications and crown ethers were no exception. Typical applications include the extraction of metal ions from effluent solutions[128], resolution of enantiomers[129], solubilisation of inorganic salts in non-polar solvents[130], and ion selective electrodes[131].

Properties of Macrocyclic Ligands

Macrocyclic entities are cyclic molecules with donor atoms (typically O, N, S or P) interspersed in an organic framework. These cyclic moieties consist of a minimum of three donor atoms within a ring of at least nine atoms. As the IUPAC names for the cyclic ether are rather complicated and too cumbersome for repeated use, abbreviated names have been implemented for ease of identification. Pedersen[127] coined the name "crown" for the cyclic polyethers because of their molecular shape and ability to encapsulate (crown) a metal ion.

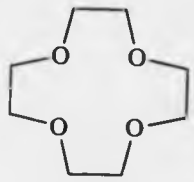
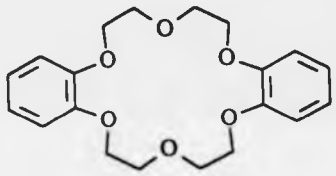
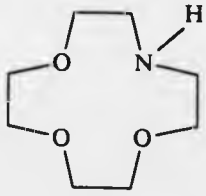
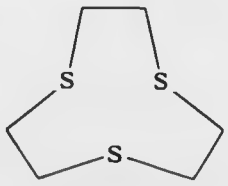
The trivial names are based on the following order of concepts,

1. number and kind of hydrocarbon rings
2. total number of atoms in the polyether ring
3. the class name 'crown'
4. the number of donor atoms in the ring.

The trivial names of some examples of the crown ethers used in this study are displayed in Table 11.

For the analogous all sulphur ligands a similar nomenclature is observed in which the word crown is replaced by the letter S. In the case of partial replacement of the oxygen atom(s) by nitrogen atoms the name of the parent ligand is assumed with the addition of a suitable prefix, monoaza, diaza *etc*.

Table 11. Schematic Representation and Trivial Names of Crown Ligands

Schematic Structure	Trivial Name
	12-crown-4
	dibenzo-18-crown-6
	monoaza-12-crown-4
	9-S-3

The sustained interest in macrocycles may be attributed to the striking stability they infer upon complexation and to the afore mentioned ability to selectively bind certain cations in preference to others. This increased stability relative to that of acyclic ligands has been termed the 'macrocyclic effect' by Cabbiness and Margerum.[132]

Additionally, macrocycles offer routes to complexes of unique structural, electronic and redox properties. The crown ether macrocycles have been found to bind with a wide variety of cations, neutral molecules and in a few specific cases with anions. The formation and stability of the resulting complex is known to be influenced by several factors including:-

1. the relative diameter of cavity in the crown and the diameter of the cation.
2. charge on the ion.
3. type of donor atoms present in ring.
4. number and position of the binding sites in ring.
5. reaction medium.
6. substituents on the macrocyclic ring.

The selectivity exerted by macrocyclic ligands for certain ions in preference to others has in part been attributed to a matching of the ionic radius to the size of the macrocyclic cavity.

Cation Radii - Cavity Size Matching

Close correspondence between cation/cavity radii frequently allows the cation to reside in the centre of the cavity thus attaining the highest stability. However formation of ion pairs is possible as the cation remains accessible from both sides

of the macrocycle, as seen in the complexes formed between dibenzo-18-crown-6 and rubidium thiocyanate.[133] (Figure 15)

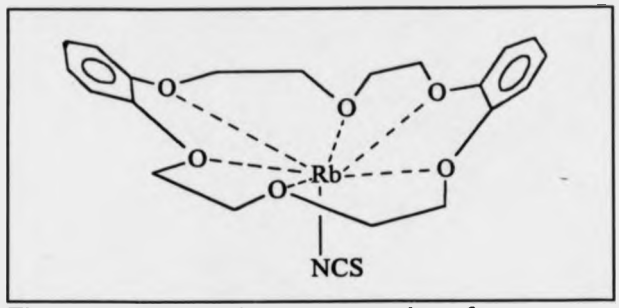


Figure 15. Schematic Representation of [DB-18-C-6·Rb(NCS)]

Cation < Cavity

Conformational adjustment of the macrocycle often alleviates the disparity between cation radii and cavity size. The small sodium ion (in conjunction with a water molecule) is able to perturb the macrocycle 18-crown-6 forcing it to support a pentagonal bipyramidal array.[134] (Figure 16)

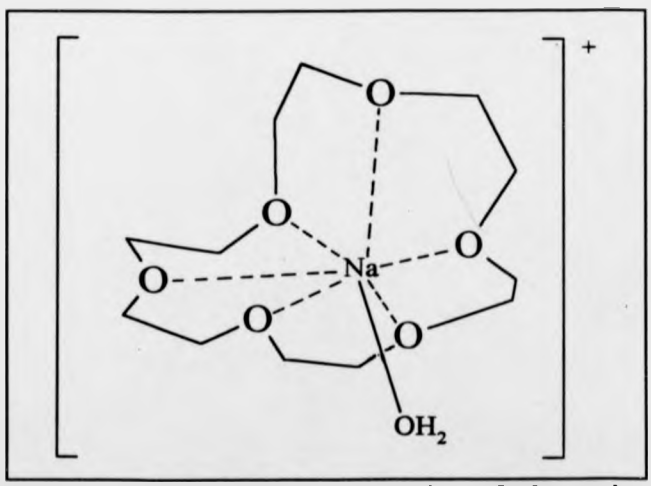


Figure 16. Schematic Representation of the cation $[Na(18\text{-}C\text{-}6)(H_2O)]^+$

Extensive ligand reorganisation can lead to 'induced' cavity formation. Pre-eminent among this class are the complexes of dibenzo-30-crown-10. The ligand is able to 'wrap' itself around cations such as potassium or rubidium so forming an 'induced' cavity.[135] (Figure 17)

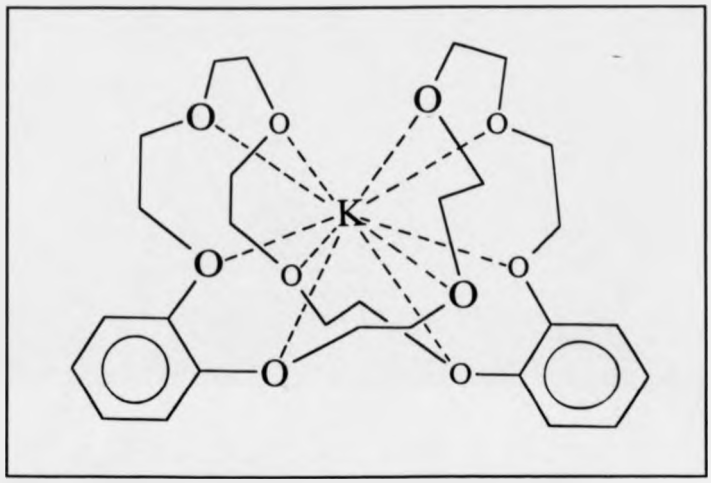


Figure 17. Schematic Representation of the cation $[K(30\text{-}C\text{-}10)]^+$

Cation > Cavity

Introducing cations of greater size than the macrocyclic cavity leads to either the cation being displaced from the mean plane of donor atoms or complex formation of a sandwich topology. Both possibilities are encountered with the ligand benzo-15-crown-5. In its reaction with potassium iodide a 2:1 sandwich structure[136] is found whilst with sodium iodide, the smaller sodium ion resides slightly above the cavity.[137]

Anion Effects

In macrocyclic complexes a cation may augment its coordination sphere with external moieties, such as solvent molecules or anions. The nature of these can greatly influence the stability of the resulting complex. The presence of an anion with the ability to coordinate to the cation can lead to formation of ion pairs, sandwich type complexes or ligand distortion. The influence exerted by the anion on the structural arrangement is particularly marked with alkaline earth metal cations. A strongly coordinating anion such as the ethylacetate anion in the K^+/18-crown-6 complex, coordinates to such an extent that the cation is displaced from the mean plane of the ring by 0.9 Å.[138] Similarly, the strongly chelating picrate anion 'levers' the sodium ion from the cavity of benzo-15-crown-5.[139]

Participation of Water Molecules

The presence of water molecules often serves to stabilise a macrocyclic complex by offering the cationic centre a further coordination site via hydrogen bonding. A demonstration of such stabilisation is evident in the complex of benzo-15-C-5 with calcium picrate, in which three water molecules complete the metal coordination sphere.[140] Inclusion of water molecules in macrocyclic complexes has also led to the formation of second sphere complexes. Here the distinguishing feature is the absence of a direct crown attachment to the metal. Instead the metal is held in a remote location through hydrogen bonding of the type $O_{crown}....H_2O....$Metal involving the coordinated water molecule(s). This coordination arrangement has been observed for a number of crown ether complexes with tin tetrahalides. A typical example is depicted in Figure 18.[141]

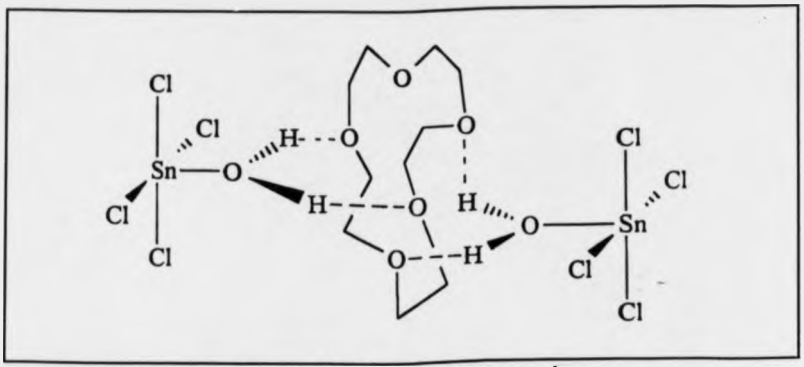


Figure 18. Schematic Representation of the unit $[(SnCl_4 \cdot H_2O)_2 \cdot 15\text{-}C\text{-}5]$

CROWN ETHERS COMPLEXES OF M(IV)

(where M=Ti, Zr, Hf and Sn)

A survey of the Daresbury Crystallographic database reveals only five crown ether complexes containing a direct metal (M = Ti, Zr or Sn) to oxygen bond, with hafnium notable by its absence.[142-145] For the general area of tin-crown ether complexes it is clear that the nature of the complex formed depends on the valence state of the metal. Although direct coordination is possible, Sn(IV) species invariably form second sphere, hydrogen bonded complexes. In such cases a complex network of hydrogen bonds links the metal indirectly to the crown ether. Smith *et al*[146] conducted a fairly comprehensive study of Sn(IV) complexes of crown ethers, isolating some fourteen examples of the general formulae $SnX_4 \cdot L \cdot 2H_2O$, $SnCl_4 \cdot L \cdot 4H_2O \cdot nCHCl_3$ (n=0 or 1), $(SnR_2X_2)_n \cdot L \cdot H_2O$ (n=1 or 2) and $(SnPh_3X)_2 \cdot L \cdot 2H_2O$, L=crown ether.

Direct interaction between Sn(IV) and a crown ether was first suggested by Gur'yanova *et al*[147] who reported the existence of the neutral adduct $2SnCl_4$(24-crown-8) in benzene solution. Unfortunately, the adduct was not isolated in the crystalline state but it was suggested that the crown ether functioned as a quadridentate donor with each tin coordinated in an exocyclic manner to two oxygen atoms from the polyether ring. Atwood *et al*[144] confirmed the existence of this mode of interaction through the structural characterisation of $SnCl_4$(18-crown-6). The analogous reaction of $TiCl_4$ with 18-crown-6 gave a structurally similar complex.[144] The compounds have a similar conformation which is depicted in Figure 19.

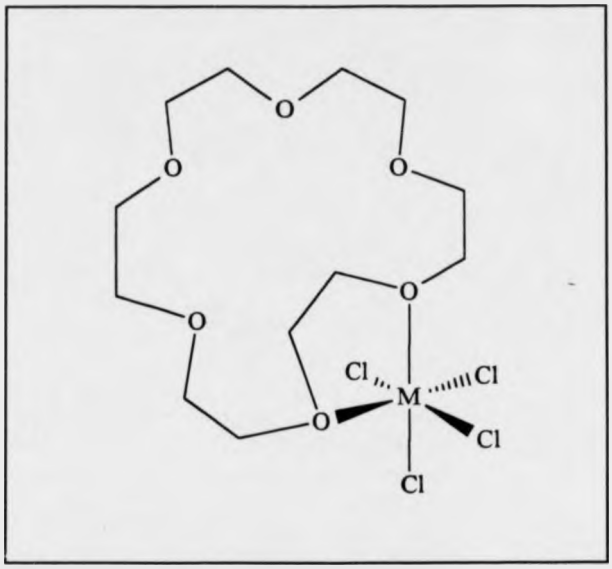


Figure 19. Schematic Representation of MCl_4(18-C-6) where M = Ti or Sn

The most immediate feature is the rare bidentate ligating mode displayed by the crown ether which has bent away from the metal species. Adopting this conformation serves to relieve the strain caused by the bidentate coordination mode, thus allowing the remaining crown backbone to reside in its preferred conformation. Prior to the isolation of these complexes Atwood *et al*[142] had paid attention to the crown ether complexation of $TiCl_3$. Reaction of $TiCl_3$ with 18-crown-6 followed by treatment with CH_2Cl_2 afforded a yellow compound. The nature of its infrared spectrum pointed towards a C_{3v} symmetry about the titanium atom, suggesting the ligand adopted a tridentate coordination mode. Inadvertent addition of water to this species during recrystallisation led to the isolation of well formed blue crystals of [$TiCl_3(H_2O)$18-crown-6]. (Figure 20)

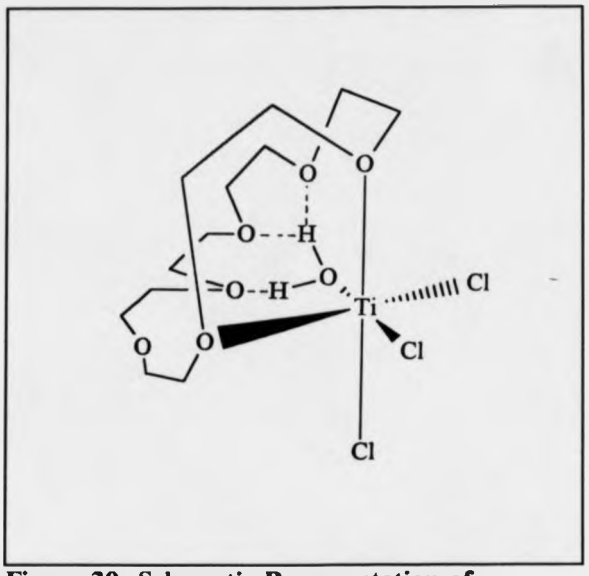


Figure 20. Schematic Representation of $[TiCl_3(H_2O)18\text{-}C\text{-}6]$

In stark contrast to the titanium and tin species discussed earlier the crown bends towards the titanium atom as a result of intramolecular hydrogen bonding with the water molecule. Although the 18-crown-6 ligand displays great flexibility both the titanium and tin atoms favour a coordination number of six at the expense of increased ligand denticity.

The 18-crown-6 ligand has many unusual interaction modes that it can adopt with metal atoms; the reaction of $ZrCl_4$ and 18-crown-6 typifies this.[143] The high Lewis acidity of $ZrCl_4$ brings about rupture of the crown ether with the formation of $[ZrCl_2(OCH_2CH_2)_5OCH_2CH_2Cl][ZrCl_5(THF)]$. The zirconium atom in this novel cation is seven coordinate. (Figure 21)

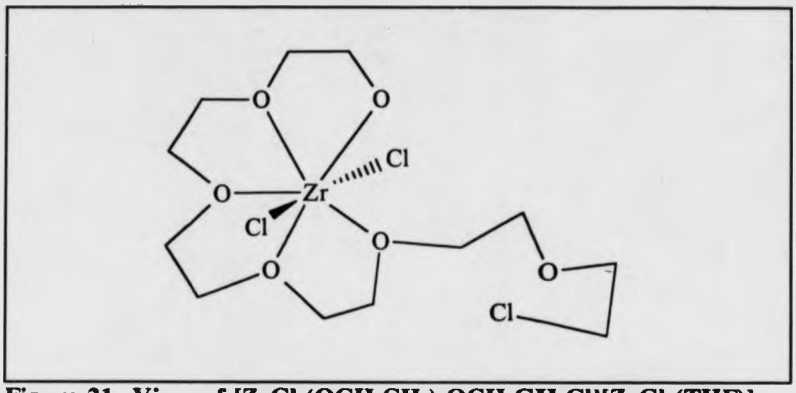


Figure 21. View of $[ZrCl_2(OCH_2CH_2)_5OCH_2CH_2Cl][ZrCl_5(THF)]$

A similar ring opening was observed for the smaller 15-crown-5 in the presence of $SnCl_4$.[148] More contemporary reports have noted this degradative behaviour in the presence of $TiCl_4$. The reaction of $TiCl_4$ with 15-crown-5 led to even greater degradation of the crown ether. This was thought to involve cleavage of an oxygen atom form the crown and formation of $TiCl_2O$. The $TiCl_2O$ unit then reacts with unchanged 15-crown-5 and $TiCl_4$ to give the complex $[TiCl(15\text{-crown-}5)(\mu\text{-}O)TiCl_3]$.[145] (Figure 22)

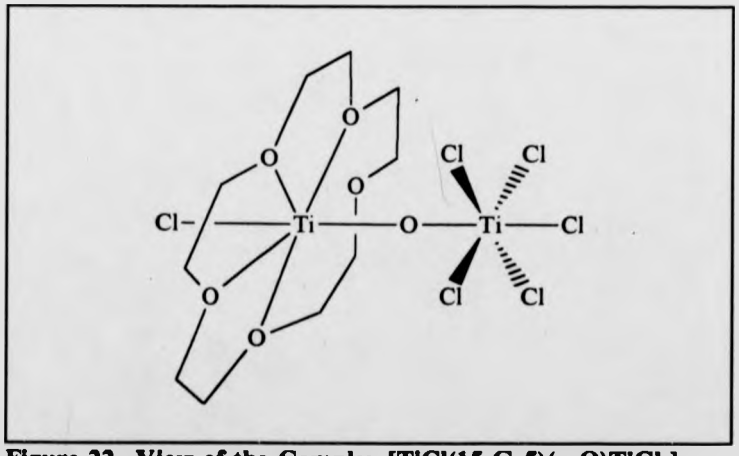


Figure 22. View of the Complex $[TiCl(15\text{-C-}5)(\mu\text{-}O)TiCl_5]$

Severe degradation is also observed in the reaction system $TiCl_4/AlCl_3$/15-C-5/THF. The preceding results suggest that degradation of the organic ligand may take place to some extent for all crown ethers when they are dissolved in the presence of strong Lewis acids. This hypothesis may be strengthened by considering the reaction of $TiCl_3$ with 15-crown-5 in the presence of $AlCl_3$. The reaction affords $[TiCl_2(15\text{-C-}5)][AlCl_4]$ and is not accompanied by any detectable degree of degradation. Further reduction in Lewis acidity by replacement of $AlCl_3$ with $MgCl_2$ leads to a pronounced increase in the stability of the 15-crown-5 moiety in the systems $TiCl_4/MgCl_2$/15-C-5 and $TiCl_3/MgCl_2$/15-C-5.[145] The reaction of these reagents can be described in terms of 'normal' complex formation and is not accompanied by any detectable degradation.

RESULTS AND DISCUSSION

The facile formation of multicomponent Ti-O bonds is a common feature of titanium chemistry. The diversity of metal halide complexes incorporating O-donor ligands,[26] homonuclear (Ti-O-Ti) and heteronuclear (Ti-O-M) oxo-bridged compounds[149] and terminal bonded (Ti=O)[150-152] complexes serves to demonstrate the high degree of Lewis acidity displayed by the metal. When combining this with the increased stability arising from the macrocyclic effect, the crown ethers (12-crown-4, 15-crown-5 and 18-crown-6) represent an 'obvious' set of potential multidentate O-donor ligands. It was envisaged that such ligands would act in concert with a more reactive positive metal centre to coerce the metal to adopt high coordination geometries. Bearing in mind the high oxophilicity of Group 4 and Sn(IV) and the increased stability of macrocyclic complexes, it is surprising to note the rarity of crown ether complexes encapsulating these metals. This course of study set out to investigate the capability of the crown ethers (12-crown-4, 15-crown-5 and 18-crown-6) to complex the titanium cation of $[TiCl_3(MeCN)_3][SbCl_6]$.

Preparation of the complexes was achieved by direct equimolar addition of the appropriate crown ether (12-crown-4, 15-crown-5 and 18-crown-6) in MeCN to the titanium cation in the same solvent. The reagent quantities are listed in Table 43. Characterisation of the compounds was effected by means of melting point measurement, microanalysis, infrared, ultra-violet and ^1H NMR spectroscopy. Unfortunately, due to a lack of solubility, only one reaction afforded crystals amenable to an X-ray diffraction study. Microanalytical and spectroscopic data can be found in Tables 44 and 45 respectively.

Reaction of $[TiCl_3(MeCN)_3][SbCl_6]$ with 12-crown-4

Dropwise addition of the crown ether in MeCN to the cation in the same solvent afforded a yellow solution. Following solvent removal a pale yellow solid was deposited. Recrystallisation from $MeCN/CH_2Cl_2$ provided large colourless block crystals. Microanalytical data was not consistent with that expected for the desired product $[TiCl_3(12\text{-}C\text{-}4)][SbCl_6]$ but with $[\{TiCl(\mu\text{-}O)(12\text{-}C\text{-}4)\}_2][SbCl_6]_2 \cdot 2CH_2Cl_2$. The structure was determined by X-ray diffraction methods.

Spectroscopic Data

Table 45 lists the bands observed between 4000-200 cm^{-1} for both the free and complexed crown ether. Upon complexation a slight shift of the ν(C-O-C) stretching vibration to a lower frequency is observed suggesting limited interaction between the metal and crown ether. Typically this shift is of 7-8 cm^{-1}. A similar reduction in ν(C-O-C) frequencies has been observed by Herber and Smelkinson[153] for a Sn(II) complex of 18-crown-6 and by Smith *et al*[146] when studying Sn(IV) crown ether complexes. The bands at 780 cm^{-1} for ν_{asym}(Ti-O-Ti) are difficult to interpret as they are complicated by the ν(C-O-C) vibration of the ligand. Similarly the ν(Ti-Cl) vibrations around 345 cm^{-1} are complicated by the ν(Sb-Cl) stretching vibration at 340 cm^{-1}.

The ^1H NMR spectrum of the product features one sharp singlet representing the crown ether. A shift of only 0.13 ppm is exhibited on complex formation suggesting there is only minimal interaction in solution. (Table 45)

X-Ray Crystallography

Following recrystallisation from $MeCN/CH_2Cl_2$ the product was obtained as large colourless block crystals. Characterisation revealed the product was not the expected $[TiCl_3(12\text{-crown-}4)][SbCl_6]$ but rather $[\{TiCl(\mu\text{-}O)(12\text{-crown-}4)\}_2][SbCl_6]_2 \cdot 2CH_2Cl_2$. The structure consists of a discrete dinuclear oxo-bridged titanium(IV) cation, two octahedral hexachloroantimonate counter anions and two molecules of CH_2Cl_2 trapped as lattice solvate. Figure 23 displays a view of the complete structure which represents the first authentic example of a crown ether chelated to titanium. Selected bond lengths and angles are listed in Table 12.

Table 12. Selected Bond Lengths (Å) and Angles (°) for $[\{TiCl(\mu\text{-}O)(12\text{-crown-}4)\}_2][SbCl_6]_2$

Ti(1)-Cl(1)	2.277)2)	Ti(1)-O(012)	1.811(3)
Ti(1)-O(1)	2.306(4)	Ti(1)-O(4)	2.237(4)
Ti(1)-O(7)	2.303(4)	Ti(1)-O(10)	2.121(4)
Ti(1)...Ti(1a)	2.789(2)	Ti(1)-O(012a)	1.823(4)
O(012)-Ti(1a)	1.823(4)	O(1)-C(2)	1.448(7)
O(1)-C(12)	1.424(8)	C(2)-C(3)	1.472(10)
C(3)-O(4)	1.423(7)	O(4)-C(5)	1.453(8)
C(5)-C(6)	1.486(8)	C(6)-O(7)	1.433(7)
C(7)-C(8)	1.433(7)	C(8)-C(9)	1.513(10)
C(9)-O(10)	1.436(6)	O(10)-C(11)	1.464(8)
C(11)-C(12)	1.498(7)		
Cl(1)-Ti(1)-O(1)	98.3(1)	O(012)-Ti(1)-O(1)	152.4(2)
Cl(1)-Ti(1)-O(4)	82.3(1)	O(012)-Ti(1)-O(4)	138.6(2)
O(1)-Ti(1)-O(4)	66.8(1)	Cl(1)-Ti(1)-O(7)	107.7(1)
O(012)-Ti(1)-O(7)	74.8(1)	O(1)-Ti(1)-O(7)	121.8(1)
O(4)-Ti(1)-O(7)	66.4(1)	Cl(1)-Ti(1)-O(10)	166.8(1)
O(012)-Ti(1)-O(10)	96.1(1)	O(1)-Ti(1)-O(10)	71.6(1)
O(4)-Ti(1)-O(10)	85.8(2)	O(7)-Ti(1)-O(10)	72.3(1)
Cl(1)-Ti(1)-O(012a)	95.9(1)	O(012)-Ti(1)-O(012a)	79.7(2)
O(1)-Ti(1)-O(012a)	75.7(1)	O(4)-Ti(1)-O(012a)	141.7(1)
O(7)-Ti(1)-O(012a)	146.8(1)	O(10)-Ti(1)-O(012a)	89.8(2)
C(2)-O(1)-C(12)	114.7(5)	Ti(1)-O(012)-Ti(1a)	100.3(2)
C(6)-O(7)-C(8)	114.7(4)	C(3)-O(4)-C(5)	118.5(4)
Cl(1)-Ti(1)-O(012)	96.5(1)	C(9)-O(10)-C(11)	113.

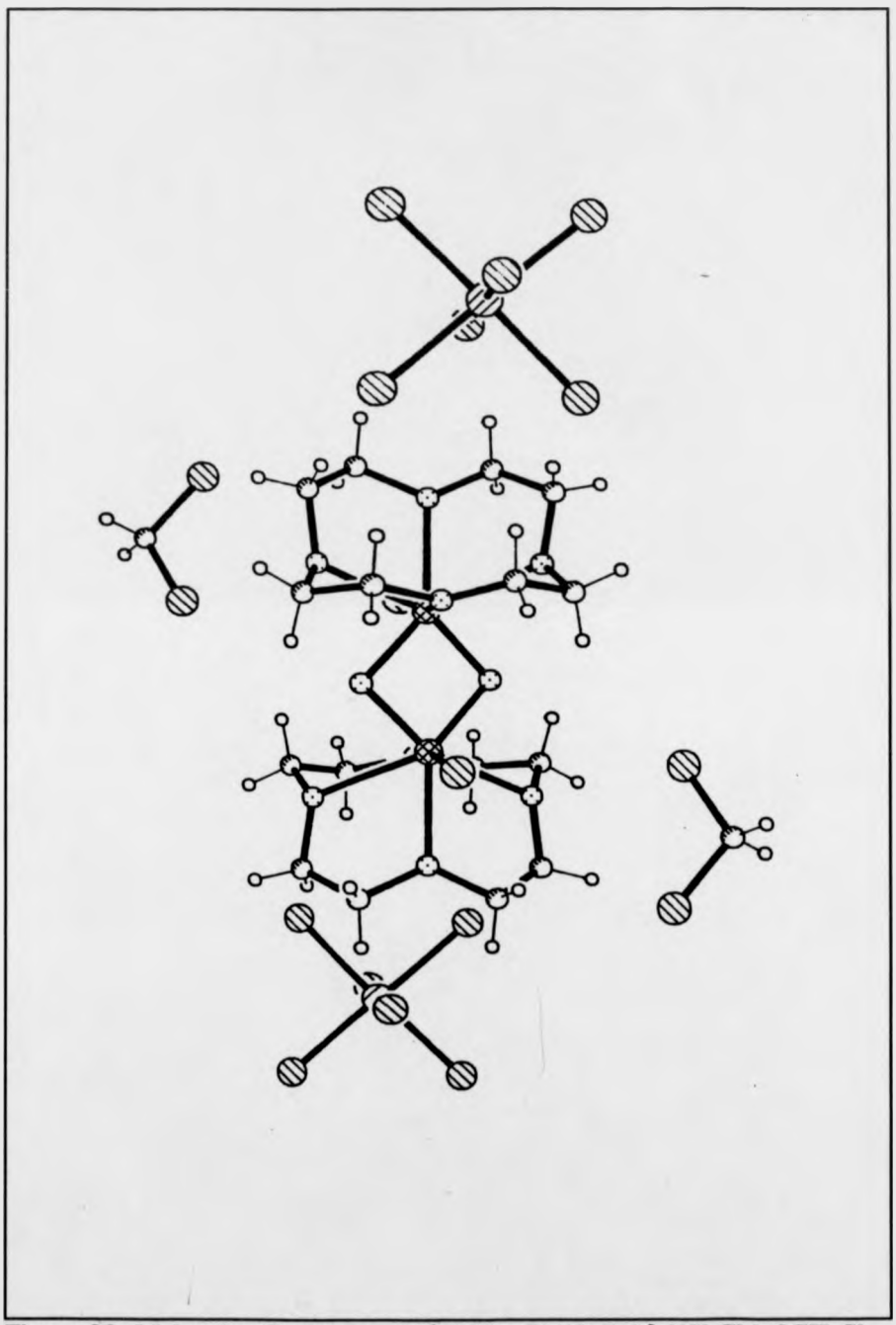


Figure 23. Molecular Structure of $[\{TiCl(\mu\text{-}O)(12\text{-}C\text{-}4)\}_2][SbCl_6]_2 \cdot 2CH_2Cl_2$

The anions are unexceptional, enjoying a regular octahedral coordination geometry around the Sb atoms, Cl-Sb-Cl mean = 90.0° and 178.7°, Sb-Cl 2.333(2)-2.376(2) mean 2.359 Å, *cf.* $[TiCl_3(MeCN)_3][SbCl_6]$[91] where the Sb-Cl distances range from 2.330(3) to 2.360(3) Å and bond angles are within 1° of the ideal. The cation depicted in Figure 24 has several interesting features that warrant further discussion.

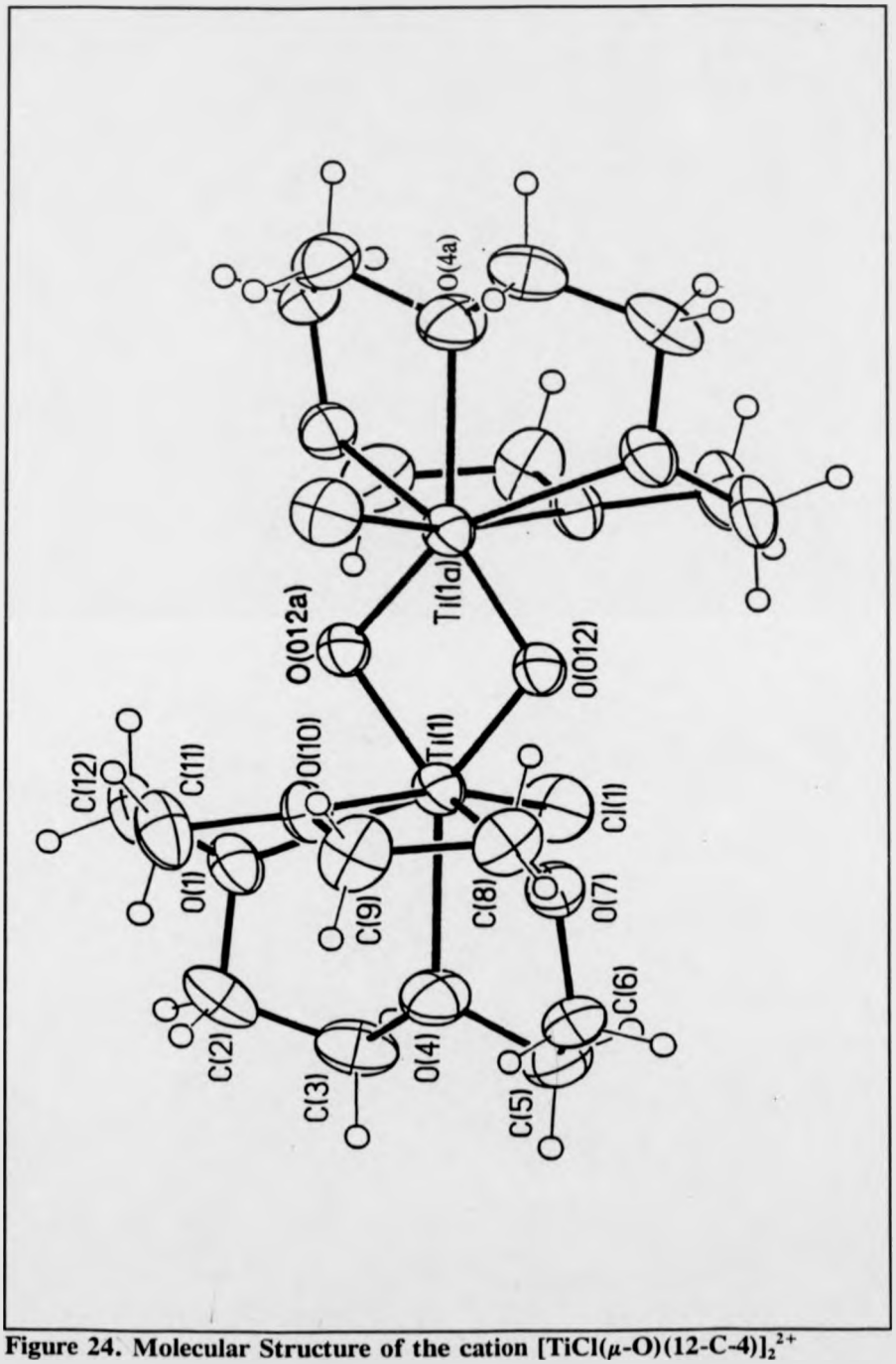


Figure 24. Molecular Structure of the cation $[TiCl(\mu\text{-}O)(12\text{-}C\text{-}4)]_2^{2+}$

The essential features are a planar Ti_2O_2 core unit and novel tetradentate oxygen chelation of a crown ether macrocycle to each of the titanium atoms, which are seven coordinate. The Ti-O_{crown} distances range from 2.121(4) to 2.237(4) Å (mean 2.242 Å) which are slightly longer than those found for $TiCl_4$(18-crown-6) 2.102(4) and 2.138(4) Å[144] and $[TiCl_3(H_2O)$18-crown-6$]\cdot CH_2Cl_2$ 2.123(8) and 2.154(4) Å.[143] Conversely the Ti-O_{core} distances 1.823(4) and 1.811(3) Å (mean 1.817 Å) are much shorter as a consequence of their multiple bond character.

Examples of complexes which feature a discrete core $Ti_2(\mu\text{-}O)_2$ unit are relatively few *viz*:-

$[\{Ti(acac)_2(\mu\text{-}O)\}_2]$ (2)[154], $K_4[Ti(O_2C_6H_4)_2(\mu\text{-}O)]_2\cdot 9H_2O$ (3)[155], $[\{Ti(OC_6H_3Pr^i_2\text{-}2,6)_2\text{-}(NC_5H_4NC_4H_8\text{-}4)(\mu\text{-}O)\}_2]$ (4)[156], $[\{TiCl[\eta^5\text{-}C_5H_2(SiMe_3)_3\text{-}1,2,4\text{-}(\mu\text{-}O)\}_2]$ (5),[157] $[\{TiCl(\mu\text{-}O)(\eta^5\text{-}Cp'')(O_2CPhMe)\}_2]$ (6),[158] $[(Ti(\eta^5\text{-}C_5Me_5)\}_2(\mu\text{-}O)_2(\sigma\text{:}\eta^5\text{-}C_5Me_4CH_2)]$ (7),[159] $[\{TiCl(\sigma\text{:}\eta^5\text{-}C_5H_4CMe_2C_5H_4N)(\mu\text{-}O)\}_2]\cdot 2CH_2Cl$ (8).[160]

The bonding dimensions of the $Ti_2(\mu\text{-}O)_2$ core units in the above compounds are listed in Table 13.

Table 13. Bond Lengths and Angles About Ti_2O_2 Cores
(CN = coordination number)

Complex	Metal CN	Ti-O (Å)	Ti...Ti (Å)	O-Ti-O (°)	Ti-O-Ti (°)	Ref
1(planar)	7	1.823(4) 1.811(3)	2.789(2)	79.7(2)	100.3(2)	This Work
2(planar)	6	1.824(4) 1.831(3)	2.729(1)	83.4(8)	96.6(2)	154
3(planar)	6	1.859(1) 1.876(1)	2.819(1)	82.0(1)	98.0(1)	155
4(planar)	5	1.865(2) 1.829(2)	2.796(1)	81.6(1)	98.4(1)	156
5(planar)	4	1.814(1) 1.835(1)	2.707(0)	84.23(3)	95.78(3)	157
6 (planar)	7	1.822(4) 1.845(3)	2.742(2)	83.2(2)	96.8(2)	158
7 (non-planar)	4	1.961(3) 1.787(3)	2.724(1)	79.9(2)	93.1(1)	159
8 (non-planar)	5	1.791(3) 1.910(2)	2.801(1)			160

The dimension of these units display a remarkable similarity despite variation in the coordination number of the metal atom, *cf*, the dimensions of complex 5 with

those of complex 1. This demonstrates the underlying rigidity of such a unit. The central Ti_2O_2 unit is exactly planar in compounds 1 to 6 with only a very small distortion from a perfect square array. Notably, in complex 1 this coplanarity is extended to include an oxygen atom, O(4) and O(4a), from each crown ether. (Figure 24)

The non-planar and unsymmetrical arrangement of the Ti_2O_2 unit in $[(Cp^*Ti)_2\text{-}\mu\text{-}(\eta^1\text{:}\eta^5\text{-}C_5\text{-}(CH_3)_4(CH_2)(\mu\text{-}O)_2]$ (7)[159] is most likely induced by the supporting methylenic $\sigma\text{:}\eta^5\text{-}C_5Me_4CH_2$ bridging ligand. The d° complexes 1-6 listed in Table 13 have metal-metal distances ranging from 2.707(0) to 2.819(1) (mean 2.768 Å) and thus lay within the bonding constraint of a typical Ti-Ti bond *cf.* 2.764-2.954 Å.[161] Despite this finding, the constraints imposed by the rigid Ti_2O_2 ring do not allow any bonding interactions.

In the present structure the coordination geometry about the titanium atoms is best viewed as a 4:3 arrangement, involving the four oxygen atoms of the crown and the chlorine plus two bridging oxygen atoms respectively. The regular zig-zag puckering of the four oxygen atoms of the crown results in deviations of:

O(1) -0.2434

O(4) +0.2595

O(7) -0.2430

and O(10) +0.2268 Å (mean deviation 0.2432 Å) from the mean plane. The titanium atom resides at a distance of 1.3520 Å from this plane and at 1.1092 Å from the plane defined by C(1),O(012),O(012a). The conformation

chosen by the crown ether results in a fairly severe distortion of the ligand. The severe staggering of the methylene hydrogens is evident from the C-C torsion angles (41.2, -44.5, -49.1, 47.8°) which display a significant disparity from the favoured gauche conformation (60°) of crown ethers.

The same 4:3 metal geometry has been encountered in the half-sandwich structures MCl_3(12-crown-4) where M = As, Sb or Bi.[162] In this instance a coplanar arrangement of the four oxygen atoms is seen with similar deviations from the ideal C-C torsion angle, typically for M = Bi 50.0 ,39.2, 43.1 and 45.0.°

Formation of $[\{TiCl(\mu\text{-}O)(12\text{-crown-}4)\}_2][SbCl_6]_2 \cdot 2CH_2Cl_2$

It is possible to rationalise the formation of the title compound from two separate viewpoints; hydrolysis or crown degradation.

Proposed Hydrolysis Route to $[\{TiCl(\mu\text{-}O)(12\text{-crown-}4)\}_2][SbCl_6]_2$

Despite rigorous drying procedures, contamination of the solvents is considered to be the most likely source of water which could promote hydrolysis during recrystallisation. The formation of the title compound is rationalised in terms of hydrolysis commencing with an 'assumed' initial adduct $[TiCl_3(12\text{-}C\text{-}4)][SbCl_6]$. (Figure 25)

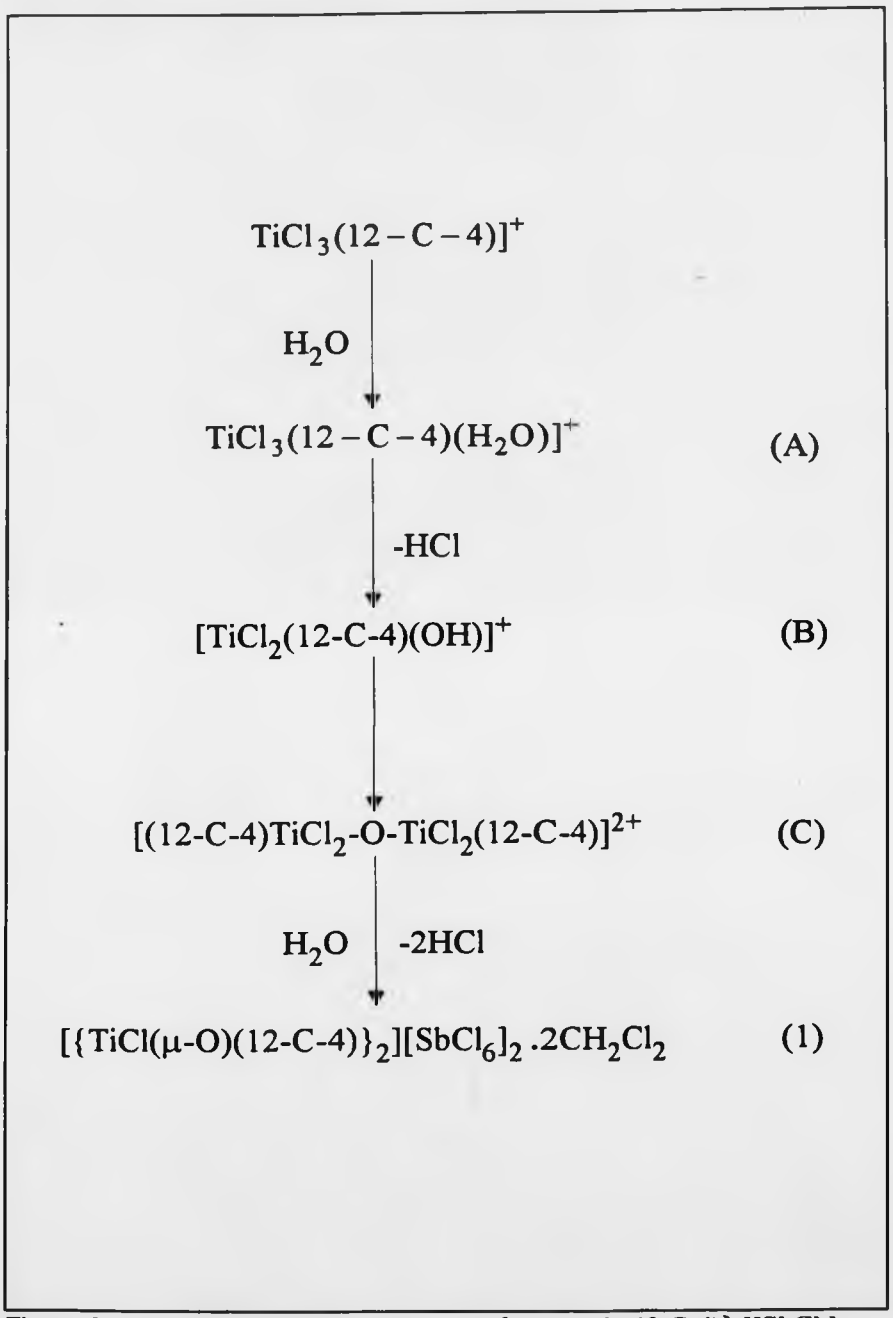


Figure 25. Proposed Hydrolysis Route to [{TiCl(μ-O)(12-C-4)}$_2$][SbCl$_6$]$_2$

The formation of two oxygen bridges rather than a single bridge is puzzling especially since the latter $Ti_2(\mu\text{-}O)$ linear unit is a more prevalent feature in titanoxane chemistry. This is found particularly, in cases where the titanium atoms carry at least one bulky substituent (such as a pentamethylcyclopentadienyl moiety).[163, 164] The work of Okuda and Herdtweck[157] concerning hydrolysis of ($TiCl_3R$) illustrates this point. Controlled hydrolysis provides both [$RCl_2Ti(\mu\text{-}O)TiCl_2R$] and [$RClTi(\mu\text{-}O)_2TiClR$] for the extremely bulky ligands R = η^5-$C_5H_2(SiMe_3)_3$-1,2,4 and η-$C_5H_2Bu^n(SiMe_3)_2$-1,2,4.

However, the presence of stray water molecules does not always lead to hydrolysis, the complex [$TiCl_3(H_2O)$18-C-6)]·CH_2Cl_2 actually crystallises with a molecule of water coordinated to the Ti(III).[142] The fact that this water molecule is involved in auxiliary hydrogen bonding to three of the remaining oxygen atoms of the 18-C-6 when taken in conjunction with the decreased polarity of a Ti^{III}-Cl *vs* Ti^{IV}-Cl bond seemingly inhibits expulsion of hydrogen chloride. Presumably, in the case of 'C' (Figure 25) the cationic nature of the titanium(IV) centres promotes further nucleophilic (H_2O) attack which, in the presence of a limited amount of water, leads directly to the title compound.

Crown Degradation

Earlier in this report, the severe crown degradation observed by the independent groups of Atwood *et al*[143] and Belsk'ii *et al*[145] was discussed. Judging from these results the outcome of the crown reactions is highly dependant on the Lewis acid character of the metal species. Introducing the Lewis acid $(TiCl_3)^+$ may be expected to cause some degree of crown fragmentation. Such behaviour would permit the isolation of our complex via the route outlined in Figure 26.

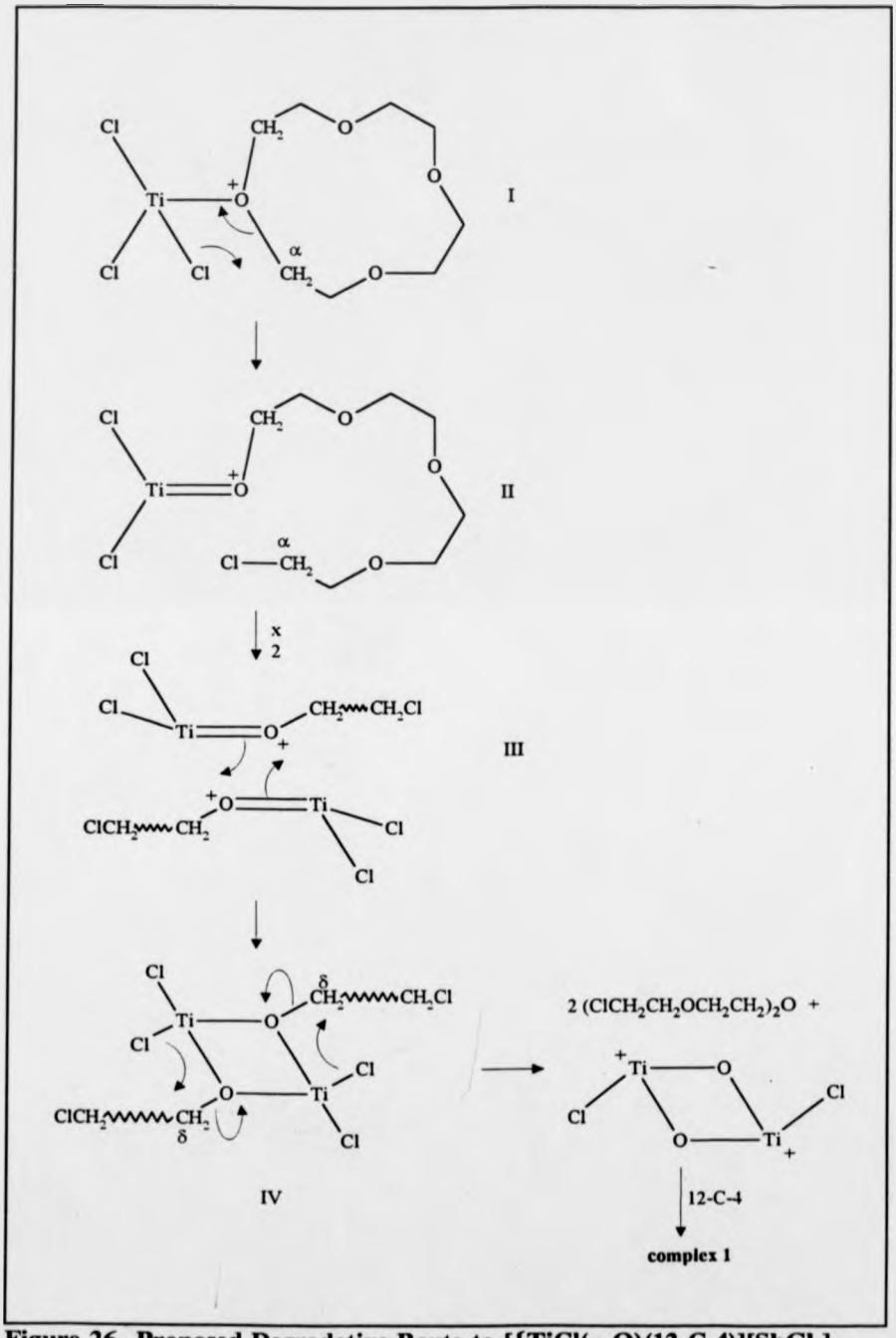


Figure 26. Proposed Degradative Route to [{TiCl(μ-O)(12-C-4)][$SbCl_6$]$_2$

The initial step proceeds with addition of the oxygen atom in a donor manner to the titanium atom forming species (I). Subsequently it is envisaged that the C-O bond cleaves with transfer of a chlorine atom to the α-C atom. In the third step the formation of two oxo bridges is suspected affording the dimer IV. Again chlorine atom transfer is envisaged (to the γ-carbon) with breakage of the C-O bond. The $[Ti_2O_2Cl_2]^{2+}$ thus formed reacts with unchanged 12-C-4 resulting in the title compound. Further crown degradation is possibly not seen as the Lewis acidity of $[Ti_2O_2Cl_2]^{2+}$ would be greatly reduced relative to the starting material. A similar pathway has been proposed in the degradative formation of $[ZrCl_2(OCH_2CH_2)_5OCH_2CH_2Cl][ZrCl_5(THF)]$, involving cleavage of 18-C-6.[143] (Figure 27)

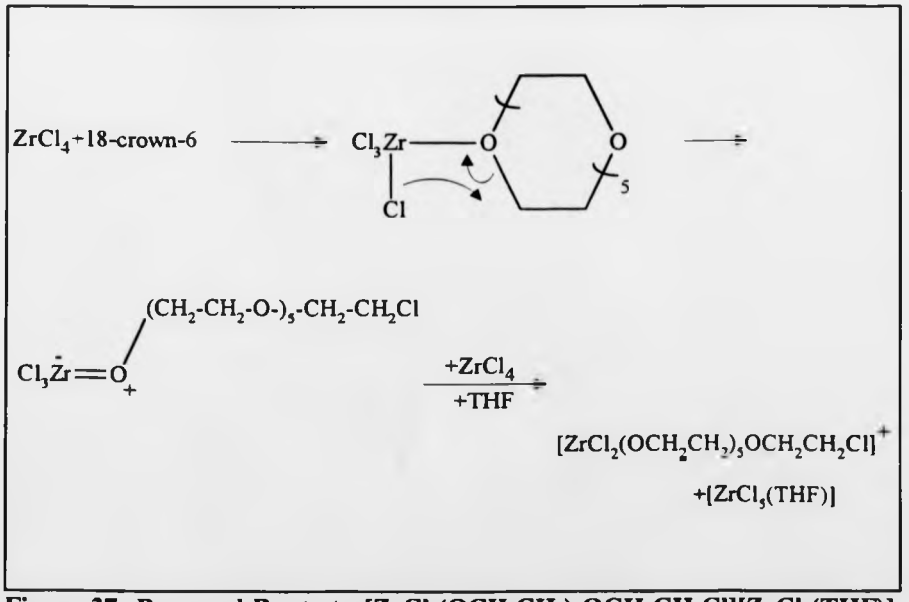


Figure 27. Proposed Route to $[ZrCl_2(OCH_2CH_2)_5OCH_2CH_2Cl][ZrCl_5(THF)]$

Reaction of $[TiCl_3(MeCN)_3][SbCl_6]$ with 15-crown-5

The reaction system yielded a semi-crystalline buff solid. It was not possible to recrystallise the sample as it was found to be insoluble in the available laboratory solvents.

Infrared Spectrum

The bands observed between 4000-200 cm^{-1} for both the free and complexed crown ether are listed in Table 45. In this instance the ligand vibrational modes of the ν(C-O-C) experience a significant shift and splitting. The bands at 1119, 1087 and 1037 cm^{-1} have shifted to 1135, 1128, 1120, 1105, 1090, 1065 and 1033 cm^{-1} with marked splitting. The symmetric ν(C-O-C) stretching band at 941 cm^{-1} is displaced to lower frequency of 936 cm^{-1}. It is difficult to draw conclusions about the effects upon Ti-O vibrations as they are coupled with the crown stretching frequencies.

Microanalysis

The results obtained point towards the isolation of a complex, containing the Ti_2O_2 core unit, which is directly related to $[\{TiCl(\mu\text{-}O)(12\text{-}C\text{-}4)\}_2][SbCl_6]_2$. For comparison the microanalytical data for both the desired $[TiCl_3(15\text{-}C\text{-}5)][SbCl_6]$ and proposed $[\{TiCl(\mu\text{-}O)(15\text{-}C\text{-}5)\}_2][SbCl_6]_2$ compounds have been calculated and are displayed in Table 14. Although consultation reveals a closer agreement with the latter compound this cannot be taken as conclusive proof of assignment.

Table 14. Microanalytical Data for $[TiCl_3(15\text{-}C\text{-}5)][SbCl_6]$ and $[\{TiCl(\mu\text{-}O)(15\text{-}C\text{-}5)\}_2][SbCl_6]_2 \cdot 2CH_2Cl_2$

Compound	Analytical Data (%) C	H	Ti
$[TiCl_3(15\text{-}C\text{-}5)][SbCl_6]$ (calc)	16.96	2.84	6.75
$[\{TiCl(\mu\text{-}O)(15\text{-}C\text{-}5)\}_2][SbCl_6]$ (calc)	18.36	3.08	7.32
$[\{TiCl(\mu\text{-}O)(15\text{-}C\text{-}5)\}_2][SbCl_6]$ (obs)	18.67	3.37	6.76

As a result of the limited spectroscopic data and absence of structural information, we can only tentatively presume the compound is $[\{TiCl(\mu\text{-}O)(15\text{-}C\text{-}5)\}_2][SbCl_6]$, for which full ligand denticity would impart a coordination number of eight upon the titanium centre.

Reaction of $[TiCl_3(MeCN)_3][SbCl_6]$ with 18-crown-6

Following solvent removal the product was obtained as a cream powder. This was recrystallised from $MeCN/CH_2Cl_2$ yielding colourless multi-faceted crystals. Microanalytical data (Table 15) was consistent with the formation of the hydrolysis product $[H_3O(18\text{-}C\text{-}6)][SbCl_6]$.

Table 15. Microanalytical Data for $[H_3O(18\text{-}C\text{-}6)][SbCl_6]$

$[H_3O(18\text{-}C\text{-}6)][SbCl_6]$	C	H	Cl
Calc (%)	23.34	4.41	34.43
Obs (%)	23.82	4.50	34.41

Spectroscopic Examination (Table 45)

The proton NMR supports this assignment with the broad singlet peak at δ 10.0 assigned to the hydronium ion protons. The crown protons give rise to a singlet at δ 3.53, (δ 3.51 for the free ligand).

Upon complexation, the IR spectrum displays ligand CH_2 rocking at 970 cm^{-1}, ν(C-C) stretching at 839 cm^{-1} and splitting of the ν(C-O-C) asymmetric stretching band into a doublet with bands at 1140 cm^{-1} and 1095 cm^{-1}. Notably, a very broad shoulder is observed at the top of the Nujol peak at 3100 cm^{-1} assigned to ν(O-H) of H_3O^+. The broad band at 345 cm^{-1} is assigned to the ν(Sb-Cl) from the hexachlorantimonate anion.

An intense charge transfer band at λ_{max} 270.1 nm was taken as further evidence of this anion.

X-ray structural analysis was not performed as hydronium ion encapsulation by crown ethers has been the subject of many reports.[165-172] The general structure of such salts is given below. (Figure 28)

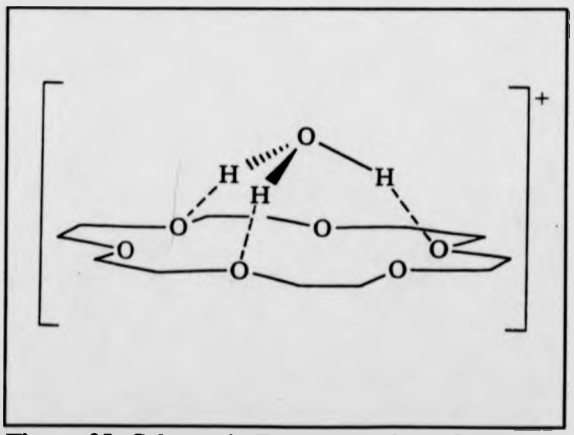


Figure 28. Schematic Representation of the cation $[(H_3O)18\text{-}C\text{-}6]^+$

CHAPTER FOUR

CROWN THIOETHERS

CROWN THIOETHERS

Before moving to discuss the results of this study, the conformational differences between crown ethers and crown thioethers will be commented upon briefly. The conformational feature of great interest to the coordination chemist is the orientation of donor atoms with respect to the central cavity. Donor atoms which point towards the cavity are described as endodentate, such as those of 18-C-6. Conversely those which point away from the cavity are exodentate, as displayed by sulphur donors in crown thioethers, with the exception of 9-S-3. The orientation provides some effective measure of the ligating behaviour of the ligands, as endodentate donors require little if any reorganisation upon complexation. The donor atom conformation adopted by crown ligands is dictated by the conformational preferences of the constituent bonds. This is rationalised by considering the nature of the 1,4-interactions at gauche, C-C-X-C and X-C-C-X units of the ligands (where X = O, S). A contrasting pattern emerges in that C-S bonds display a marked preference for gauche placement whilst C-O invariably adopt anti placement.

These opposite conformational preferences are exemplified by examining the bonds of hexathia-18-crown-6[173] and 18-crown-6.[174] In the latter example only two out of the twelve C-O bonds adopt gauche placement contrasting sharply with the sulphur analogue in which all twelve C-O bonds have gauche placement. These opposite conformational preferences are greatly influenced by the difference in the C-X bonds lengths compare X = O 1.43 Å and X = S 1.82 Å. Mark and Flory[175] noted that gauche placement at CH_2CH_2-O-CH_2 units dictated a separation of 1.8 Å for the terminal hydrogen atoms causing significant repulsion. (Figure 29)

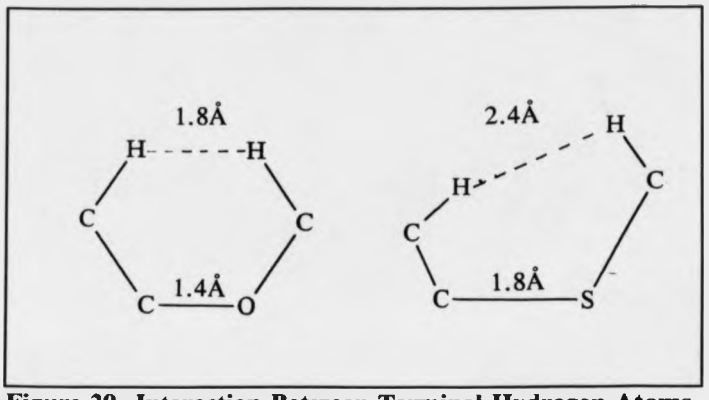


Figure 29. Interaction Between Terminal Hydrogen Atoms

Similar, opposite conformational preferences are also observed at the gauche placement of X-C-C-X bonds. In this instance the O-C-C-O prefers gauche placement whilst S-C-C-S adopt anti placement where the larger size of the sulphur atom causes greater electron-electron repulsion, destabilising a gauche placement. This preference for gauche placement is expressed by crown thioethers in general. Of those under investigation in this study both 12-S-4 and 15-S-5 steadfastly obey these conformational rules.[176, 177] The crystal structure of 12-S-4 was obtained by Robinson *et al*[176] in 1988 revealing all sulphur atoms are located at the corners of a square with all eight C-S bonds adopting gauche placement. (Figure 30)

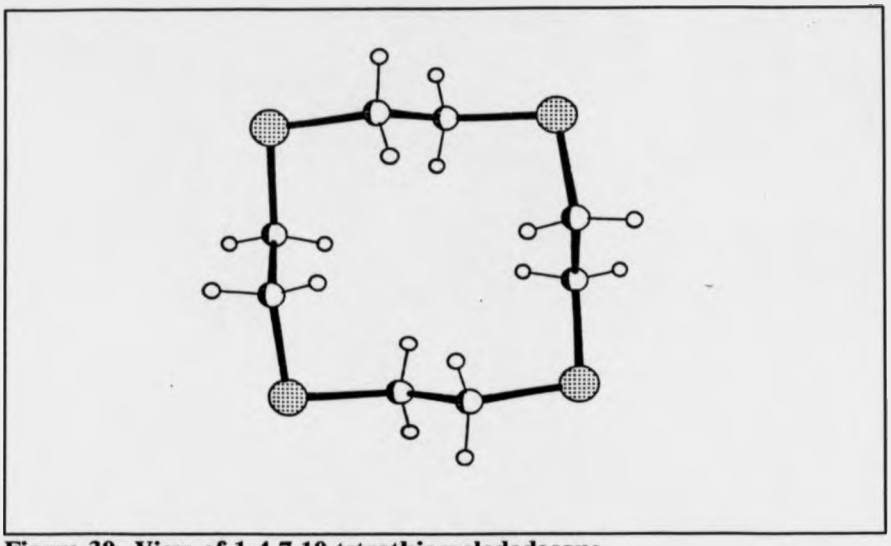


Figure 30. View of 1,4,7,10-tetrathiacyclododecane

Similarly, the crystal structure of 15-S-5 shows that each sulphur is exodentate.[177] (Figure 31)

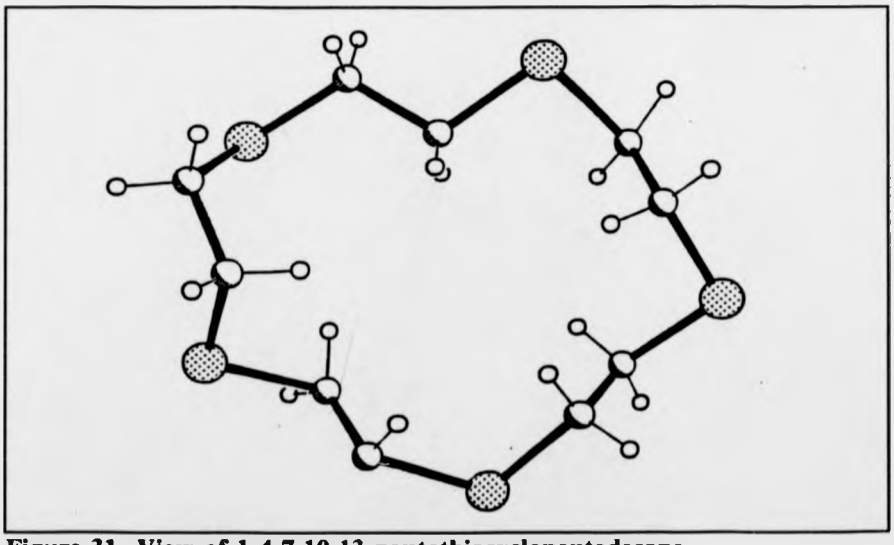


Figure 31. View of 1,4,7,10,13-pentathiacyclopentadecane

In contrast to the previous structures, that of 18-S-6 violates the exo generalisation in having two of the six sulphur atoms pointing into the central cavity.[173] (Figure 32)

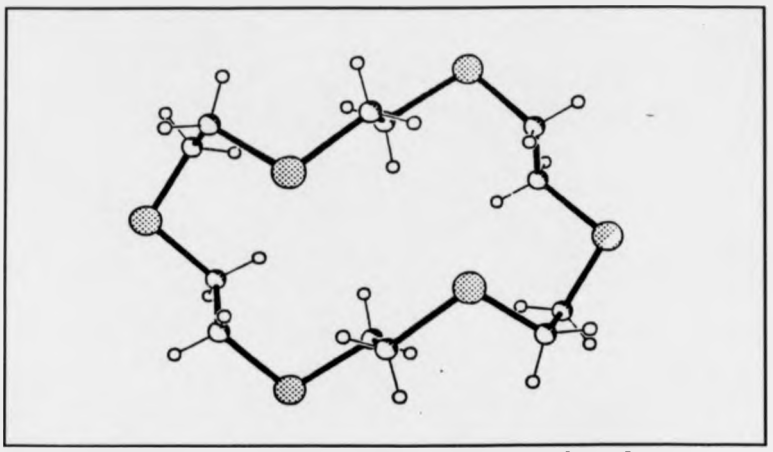


Figure 32. View of 1,4,7,10,13,16-hexathiacyclohexadecane

The ligand 9-S-3 is of particular interest as it has a triangular configuration in which endodentate sulphur atoms are preorganised for facial coordination to an octahedral face.[178] (Figure 33)

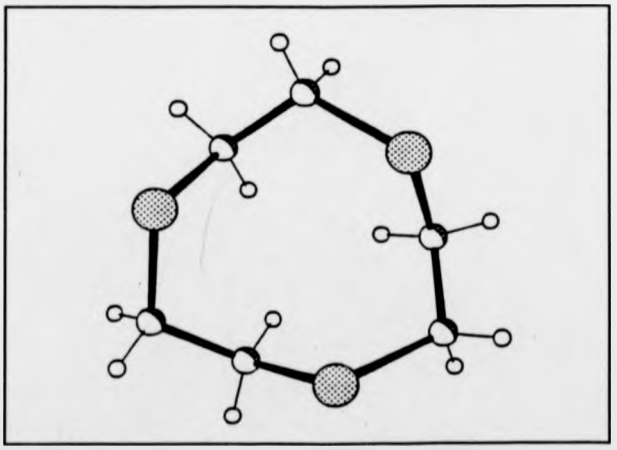


Figure 33. View of 1,4,7-trithiacyclononane

The objective of this study was to evaluate the complexing abilities of the crown thioether series 9-S-3, 12-S-4, 15-S-5 and 18-S-6 with $[TiCl_3(MeCN)_3][SbCl_6]$ and MCl_4 where M = Ti, Zr, Hf and Sn. This investigation was seen as a useful contrast to the study of their oxygen donor counterparts. The apparent lack of interest in early transition metal crown thioether complexes may stem from the preconceived 'mismatch' of these typecast 'hard' metal ions with the 'soft' S-donors. Yet there are examples in the literature which seem to refute this. Surprisingly, Olmstead *et al*[179] have reported the structure of the six coordinate Ti(IV) complex $[TiCl_3(C_6H_{11}OS_2)]$ involving the tridentate [O, S, S'] ligand, 1,5-dithiacyclocta-3-ol. More recently, the half 'sandwich' type, six coordinate vanadium(IV) complex $[VOCl_2(9\text{-}S\text{-}3)]$ has been isolated in which the trithiamacrocycle functions in its normal terdentate binding mode.[180] Other supportive evidence for favourable S-donation to 'hard' metal centres such as M(IV) (M=Ti, Zr and Hf) can be found in the literature. The ambidentate ligand thioxane prefers to bind to $TiCl_4$ through the sulphur atom rather than the oxygen atom.[181] Furthermore, all metal tetrachlorides (M = Ti, Zr, Hf and Sn) form well characterised complexes with tetrahydrothiothene[182] and Ti(IV) with 1,4-dithiane[183] and dimethylthioether.[184] Interestingly, the hafnium adduct of tetrahydrothiophene was found to be more stable than the related zirconium adduct, indicating a slightly diminished 'hard' character for Hf(IV) compared to zirconium.

These results, in spite of unfavourable HSAB predications, encouraged our investigation of similar S-donation to some 'hard' Group 4 species (M=Ti, Zr and Hf) and also (for comparison) M=Sn(IV).

RESULTS AND DISCUSSION

Initial studies concentrated on the substitution reactions of the cation $[TiCl_3(MeCN)_3]^+$, in which it was hoped the macrocycle 9-S-3 would replace the monodentate MeCN ligands. The positive charge and the d^0 electron configuration of Ti(IV) in $[TiCl_3(MeCN)_3]^+$ result in this species being typecast as 'hard' and not particularly suited for sulphur coordination. In addition the complexing ability of the crown thioethers, 9-S-3, 12-S-4, 15-S-5 and 18-S-6, with neutral metal chlorides (MCl_4 M=Ti, Zr, Hf and Sn) was assessed.

Reaction of $[TiCl_3(MeCN)_3][SbCl_6]$ with 9-S-3

The reaction of $[TiCl_3(MeCN)_3][SbCl_6]$ with 9-S-3 gave an intractable brown residue which was not pursued, and a small quantity of maroon crystals. From the analytical and spectroscopic data (Page 154) it became clear that the product was neither a Ti(IV) nor a Ti(III) species and, in the absence of an 'obvious' identification, the X-ray crystal structure was determined. Recognition of the anion as $[Sb_2Cl_8]^{2-}$ based on Sb(III) necessitated an $[M(9\text{-}S\text{-}3)_2]^{2+}$ cation. A check of the bond dimensions and associated crystal structure data led to the metal ion being identified as iron by comparison with $[Fe(9\text{-}S\text{-}3)_2][PF_6]_2$. (Table 16) The redox system outlined in Equation 23 was presumably facilitated by a flaw in the stainless steel transfer tube used to manipulate the acetonitrile solution of $[TiCl_3(MeCN)_3][SbCl_6]$ within the Schlenk system.

$$Fe^{\circ} + [Sb^{V}Cl_6]^{-} \rightarrow [Sb^{III}Cl_4]^{-} + Fe^{II} + 2Cl^{-} \qquad (23)$$

In order to test the validity of this, the proposed reaction was mimicked using iron filings, affording a satisfactory yield of the product. (Equation 24)

$$2Fe^{\bullet} + 2SbCl_5 + 2(9\text{-}S\text{-}3) \rightarrow [Fe(9\text{-}S\text{-}3)_2][Sb_2Cl_8] + 2Cl^- + Fe^{2+} \quad (24)$$

The structures of the discrete cation $[Fe(9\text{-}S\text{-}3)_2]^{2+}$ obtained in this study and the polymeric chain of $[Sb_2Cl_8]^{2-}$ anions are displayed in Figure 34 with relevant atom labelling.

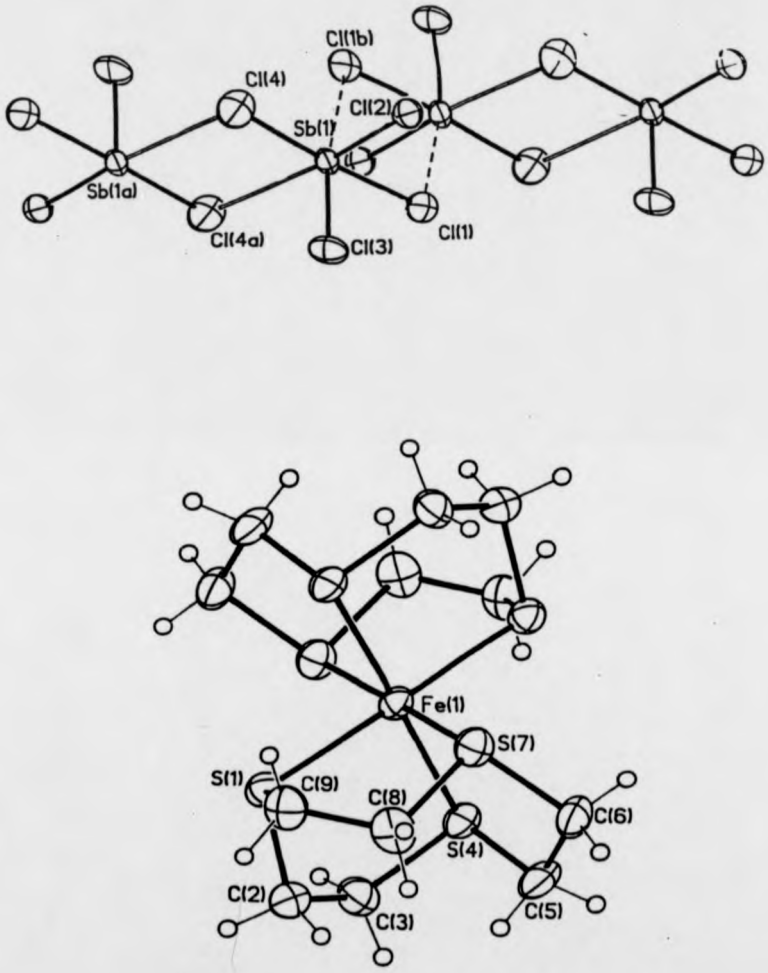


Figure 34. Molecular Structure of $[Fe(9\text{-}S\text{-}3)_2][Sb_2Cl_8]$

As noted above, the cation has been reported by Weighardt *et al*[185] as the red salt $[Fe(9\text{-}S\text{-}3)_2][PF_6]$ and features two crown thioether ligands facially coordinated to the metal centre imposing a six coordinate geometry. The bond lengths and angles of this compound are listed alongside those of $[Fe(9\text{-}S\text{-}3)_2][Sb_2Cl_8]$ for comparative purposes. (Table 16)

Table 16. Bond length data for 9-S-3 Complexes with Fe^{II}

Feature	Weighardt (185)	**This work**
Fe-S (Å)	2.25	2.25
S-Fe-S (°)	90.0	89.9
C-C (Å)	1.51	1.52
C-S (Å)	1.83	1.82

The main point of interest focuses upon the structure of the anion which is composed of dimeric $[(Sb_2Cl_8)]^{2-}$ units linked by weak chlorine bridges forming polymeric chains. Within the dimeric unit each antimony exhibits a distorted octahedral geometry with three terminal Sb-Cl bonds, 2.574(3), 2.434(3), 2.382(2) Å and two bridging Sb-Cl bonds 2.727(3), 2.959(3) Å over a centre of symmetry. Linkage of units via a further weak bridging contact, Sb(I).....Cl(1b) 3.345 Å, results in a polymeric chain. (Figure 34)

The differing steric requirements of the terminal and bridging atoms are reflected in their Cl-Sb-Cl bond angles, *cf.* $Cl^t(2)$-Sb(1)-$Cl^t(3)$ 90.2(1)° *vs* $Cl^b(4)$-Sb(1)-$Cl^b(4a)$ 80.8(1)°. Similarly, the angle Cl(1)-Sb(1)-Cl(4) 174.7° is essentially linear whereas Cl(3)-Sb(1)-Cl(1b) 160.2(1)° is extensively distorted away from the 180° line of the presumed lone pair of electrons associated with the Sb(III)

centre. A somewhat similar polymeric chain structure showing a *fac* arrangement of three short Sb-Cl bonds around each distorted octahedral Sb(III) centre has been observed for the magnesium(II) salt $[Mg(MeCN)_6][Sb_2Cl_8]$.[186]

Reaction of Covalent MCl_4 Metal Chlorides (M=Ti, Zr, Hf and Sn) with Crown Thioethers

The reactions were carried out in a similar manner using a specially adapted U-shaped Schlenk vessel. The synthetic details can be found in Table 47.

Titanium Tetrachloride

The U-shaped vessel was charged to approximately half capacity with MeCN ($25cm^3$). A solution of $TiCl_4$ in MeCN was added dropwise to one side-arm and coincidentally, a solution of 9-S-3 in the same solvent added to the other arm. The layer of MeCN serves as a 'buffer' thereby retarding inital contact/reaction between the two reagents. After several days yellow dendritic crystals were deposited. Their small size did not permit structural characterisation and unfortunately attempts with other solvents did not induce a change in crystal habit. Analytical data supported a 1:1 stoichiometry, $TiCl_4$(9-S-3), whilst the IR data favours one of several possible structural arrangements displayed in Figures 35 and 36.

The bands observed at 1409, 1020, 938, 905 and 780 cm^{-1} are characteristic of the crown thioether ligand whilst six bands are observed in the far IR region. Such an IR pattern is in accord with neutral adduct formation involving a six coordinate metal (C_{2v}), as the enforced *cis* placement of two sulphur atoms requires four ν(Ti-Cl) bands and two ν(Ti-S) bands. (Figure 35) Whilst the favoured octahedral geometry of titanium is attained, this structural arrangement is at odds with the preorganised conformation of the donor atoms. However, this ligand appears to have sufficient flexibility to permit this arrangement. A similar example of bidentate chelation of 9-S-3 is provided by the square based pyramidal

complex $[Pt(9\text{-}S\text{-}3)_2]^{2+}$.[187] In this case, one of the macrocyclic ligands exhibits a conformation in which a sulphur atom points away from the central metal ion, resisting any bonding interactions, Pt...S 4.04 Å.

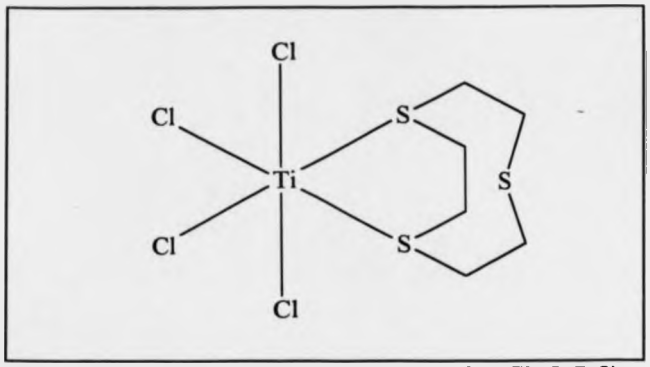


Figure 35. Schematic Representation of $TiCl_4(9\text{-}S\text{-}3)$

Alternatively, a coordination number of six is possible via the expulsion of a chloride ion. (Figure 36) However, on the basis of the poor σ-donor ability of crown thioethers there would be very little tendency for the metal to relinquish a chloride ion. This arrangement is also ruled out as the symmetry of the cation (C_{3v}) would require only four IR active bands in the far IR region.

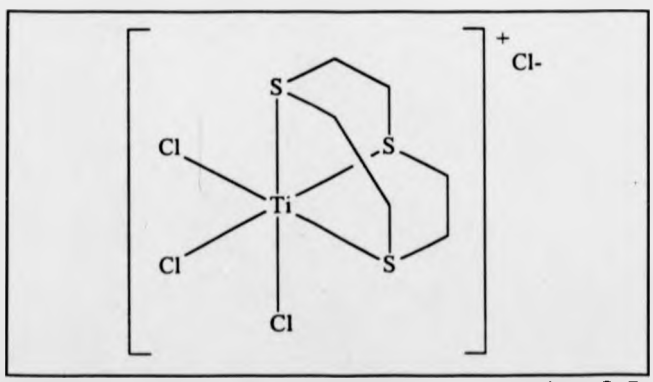


Figure 36. Schematic Representation of $[TiCl_3(9\text{-}S\text{-}3)][Cl]$

$SnCl_4$ Crown Thioether Complexes

Reactions of the crown thioethers, 9-S-3 and 18-S-6, with $SnCl_4$ in standard Schlenk vessels afforded precipitates which were insoluble in all available solvents. Their reactions in the U-shaped vessel provided the first examples of $SnCl_4$ complexed by crown thioethers, in the form of the compounds $[SnCl_3(9\text{-}S\text{-}3)]_2[SnCl_6]$ and $2SnCl_4 \cdot 18\text{-}S\text{-}6$. The products were deposited as small colourless crystals and were characterised by IR (Table 49), elemental analysis (Table 17) and X-ray diffraction studies.

No reaction was observed between $SnCl_4$ and either 12-S-4 or 15-S-5.

Table 17. Microanalytical Data for $SnCl_4$ Complexes with 9-S-3 and 18-S-6

Compound	C	H	Cl	N
	calc/obs (%)			
$[SnCl_3(9\text{-}S\text{-}3)]_2[SnCl_6]$	12.61	2.12	37.26	/
	12.44	2.09	37.07	/
$2SnCl_4 \cdot 18\text{-}S\text{-}6$	18.22	2.95	30.74	1.52
	18.09	2.92	30.29	1.75

Reaction of $SnCl_4$ with 9-S-3

X-Ray Crystallography

The compound has the empirical formula $3SnCl_4 2(9\text{-}S\text{-}3)$. The structure consists of discrete $[SnCl_3(9\text{-}S\text{-}3)]^+$ cations and $[SnCl_6]^{2-}$ anions in the ratio 2:1. The bond lengths and bond angles are listed in Table 18.

Table 18. Selected Bond Lengths (Å) and Angles (°) for $[SnCl_3(9\text{-}S\text{-}3)]_2[SnCl_6]$

Sn(1)-Cl(2)	2.366(4)
Sn(1)-Cl(3)	2.369(3)
Sn(1)-Cl(1)	2.371(4)
Sn(1)-S(4)	2.618(3)
Sn(1)-S(7)	2.636(3)
Sn(1)-S(1)	2.657(4)
Cl(2)-Sn(1)-Cl(3)	98.79(13)
Cl(2)-Sn(1)-Cl(1)	101.38(13)
Cl(3)-Sn(1)-Cl(1)	95.40(13)
Cl(2)-Sn(1)-S(4)	86.93(12)
Cl(3)-Sn(1)-S(4)	86.97(12)
Cl(1)-Sn(1)-S(4)	170.87(14)
Cl(2)-Sn(1)-S(7)	86.76(12)
Cl(3)-Sn(1)-S(7)	169.60(12)
Cl(1)-Sn(1)-S(7)	92.10(13)
S(4)-Sn(1)-S(7)	84.54(11)
Cl(2)-Sn(1)-S(1)	165.88(12)
Cl(3)-Sn(1)-S(1)	90.01(12)
Cl(1)-Sn(1)-S(1)	88.67(13)
S(4)-Sn(1)-S(1)	82.51(11)
S(7)-Sn(1)-S(1)	82.94(11)

The anion warrants only a brief mention as it is unexceptional and displays an almost perfect octahedral geometry. This is evident from the bonding dimensions, Sn-Cl (mean) 2.4485 Å, Cl-Sn-Cl (mean) 88.83-91.17° and 179.997-180.0°.

The cation, which is illustrated in Figure 37 with atom labelling, provides a classic example of *fac* coordination of 9-S-3 to a $SnCl_3^+$ unit with resulting near perfect octahedral metal geometry.

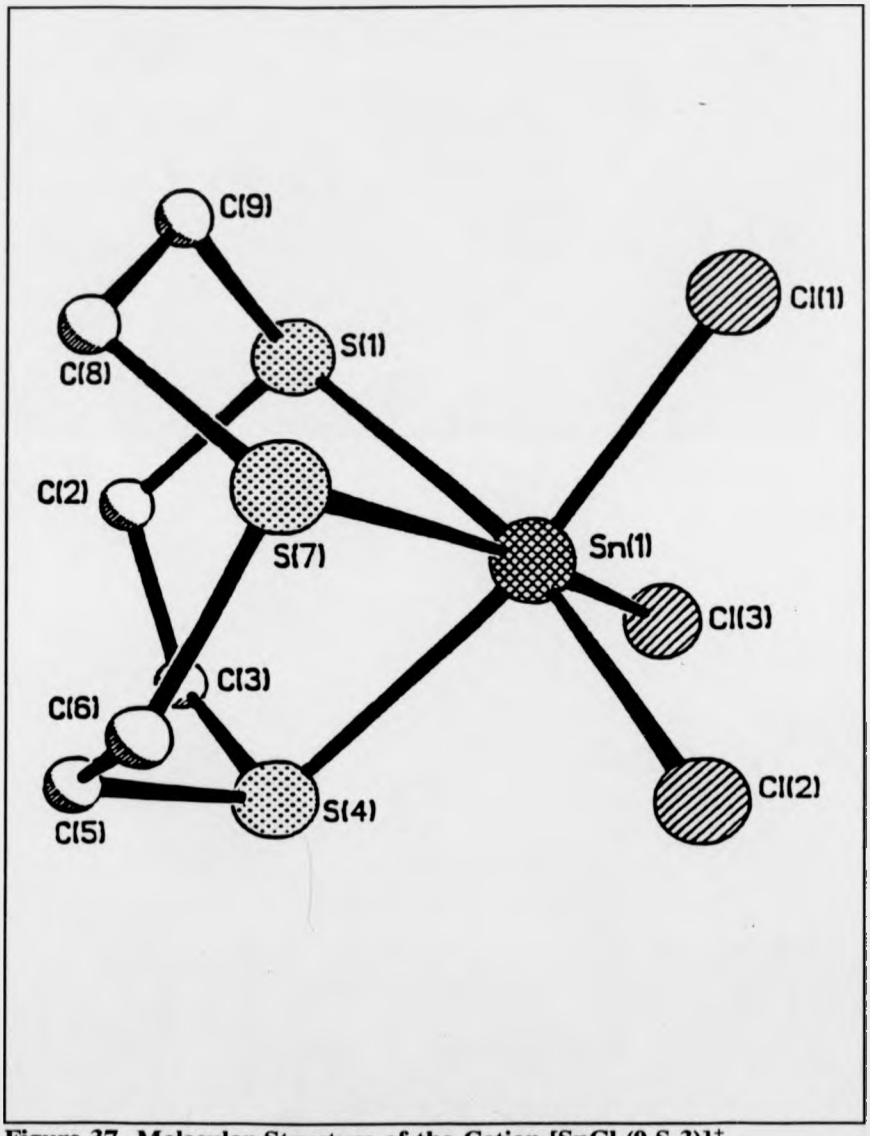


Figure 37. Molecular Structure of the Cation $[SnCl_3(9\text{-}S\text{-}3)]^+$

It is interesting to note that this cation is most likely formed via the expulsion of a chloride anion upon coordination of the crown thioether. This is a rare occurrence as the low σ-donor ability of crown thioethers seldom permits halide expulsion. However, in this example the favoured hexa-coordination of Sn(IV) and the exodentate conformational preference of the ligand are seen to act in unison to afford a six-coordinate cationic species as opposed to a neutral adduct exhibiting a coordination number of seven.

The Sn-Cl bond distances (mean 2.369 Å) exhibited by this rare example of a tin(IV) cation, $[SnCl_3]^+$, are equivalent and show the shortening expected for a cationic species when compared with the neutral *bis*-adducts: $SnCl_4$(1,5-DTCO)$_2$ DTCO = dithiacyclooctane, (mean 2.421 Å),[60] and $SnCl_4$(detu)$_2$ detu = 1,3-diethylthiourea, (mean 2.43 Å).[58] Similarly the Sn-S bond lengths display a close correspondence. This is most likely due to the symmetrical arrangement of the terdentate 9-S-3 and the trio of halogen atoms around the central metal ion. The 9-S-3 ligand imposes an angular constriction (S-Sn-S mean 83.3 Å) which is counterbalanced by a corresponding angular dilation about the halogen atoms (Cl-Sn-Cl mean 98.6 Å). Similar macrocyclic dilation and constriction have previously been noted in $[VOCl_2(9\text{-}S\text{-}3)]$[180] and $[ReO_3(9\text{-}S\text{-}3)]$.[188]

Table 19. Comparison of Bond Angles of Selected 9-S-3 Complexes

Compound	S-M-S (°)	Cl-M-Cl (°)
$[SnCl_3(9\text{-}S\text{-}3)]_2[SnCl_6]$	83.3	98.6
$[VOCl_2(9\text{-}S\text{-}3)]$[180]	81.0	95.0
$[ReO_3(9\text{-}S\text{-}3)]$[188]	79.5	107.4

Examination of the C-C and C-S torsion angles around the ring reveals a regular a gga gga gg pattern implying minimal strain. (a=anti, g=gauche)

Table 20. Torsion Angles for $[SnCl_3(9\text{-}S\text{-}3)]_2[SnCl_6]$

Torsion Angle	(°)
C(3)-S(4)-C(5)-C(6)	-132.99(1.00)
S(4)-C(5)-C(6)-S(7)	60.69(1.24)
C(5)-C(6)-S(7)-C(8)	54.77(1.10)
C(6)-S(7)-C(8)-C(9)	-127.12(0.88)
S(7)-C(8)-C(9)-S(1)	53.59(1.22)
C(8)-C(9)-S(1)-C(2)	59.46(1.11)
C(9)-S(1)-C(2)-C(3)	-131.22(0.95)
S(1)-C(2)-C(3)-S(4)	55.38(1.24)
C(2)-C(3)-S(4)-C(5)	55.52(1.13)

The regularity of C-C bond lengths (mean 1.54 Å) and C-S bond lengths (mean 1.84 Å) correlates with the regular pattern of torsion angles around the ring. The central metal atom does not reside in the central cavity as may be expected but is displaced by 1.6895 Å from the plane defined by the three sulphur atoms and by 1.1437 Å from that of the three chlorine atoms.

IR Data

Although the crown thioether complex remains six coordinate its IR spectrum differs significantly from that of the adduct $SnCl_4(MeCN)_2$, demonstrating the marked change in the environment about the tin centre upon complexation with 9-S-3. The IR spectrum of $SnCl_4(MeCN)_2$ displays a single broad band in the far IR region, whilst that of the product displays four bands; 661w, 436m, 345vs, (br), 295vs, (br) cm^{-1}. This is in agreement with C_{3v} symmetry which predicts two ν(Sn-Cl) and two ν(Sn-S) IR active bands.

Reaction of $SnCl_4$ with 18-S-6

The reaction afforded the product as small colourless cubic crystals.

X-Ray Crystallography

The structure was confirmed as $2SnCl_4 \cdot 18\text{-S-}6$ and is displayed in Figure 38 with the relevant atom labelling. The bond lengths and angles are included in Table 21.

Table 21. Selected Bond Lengths (Å) and Angles (°) for $2SnCl_4 \cdot 18\text{-S-}6$

Sn(1)-Cl(3')	2.30(2)
Sn(1)-Cl(4)	2.31(2)
Sn(1)-Cl(3)	2.38(2)
Sn(1)-Cl(2)	2.391(2)
Sn(1)-Cl(1)	2.421(2)
Sn(1)-Cl(4')	2.42(2)
Sn(1)-S(4)	2.535(10)
Sn(1)-S(7')	2.56(2)
Sn(1)-S(7)	2.687(13)
Sn(1)-S(4')	2.689(13)
S(1)-C(2)	1.81(2)
C(2)-C(3)	1.64(3)
C(3)-S(4)	1.81(2)
S(4)-C(5)	1.80(2)
C(5)-C(6)	1.48(2)
C(6)-S(7)	1.85(3)
S(7)-C(8)	1.87(2)
C(8)-C(9)	1.68(2)
C(9)-S(10)	1.82(2)
N(31)-C(31)	1.13(2)
C(31)-C(32)	1.56(2)
Cl(4)-Sn(1)-Cl(3)	97.3(7)
Cl(4)-Sn(1)-Cl(2)	96.7(5)
Cl(3)-Sn(1)-Cl(2)	91.5(5)
Cl(4)-Sn(1)-Cl(1)	93.2(5)
Cl(3)-Sn(1)-Cl(1)	94.3(5)
Cl(2)-Sn(1)-Cl(1)	167.85(8)
Cl(4)-Sn(1)-S(4)	92.1(7)
Cl(3)-Sn(1)-S(4)	169.4(6)
Cl(1)-Sn(1)-S(4)	90.0(4)
S(4)-Sn(1)-S(7)	83.8(5)

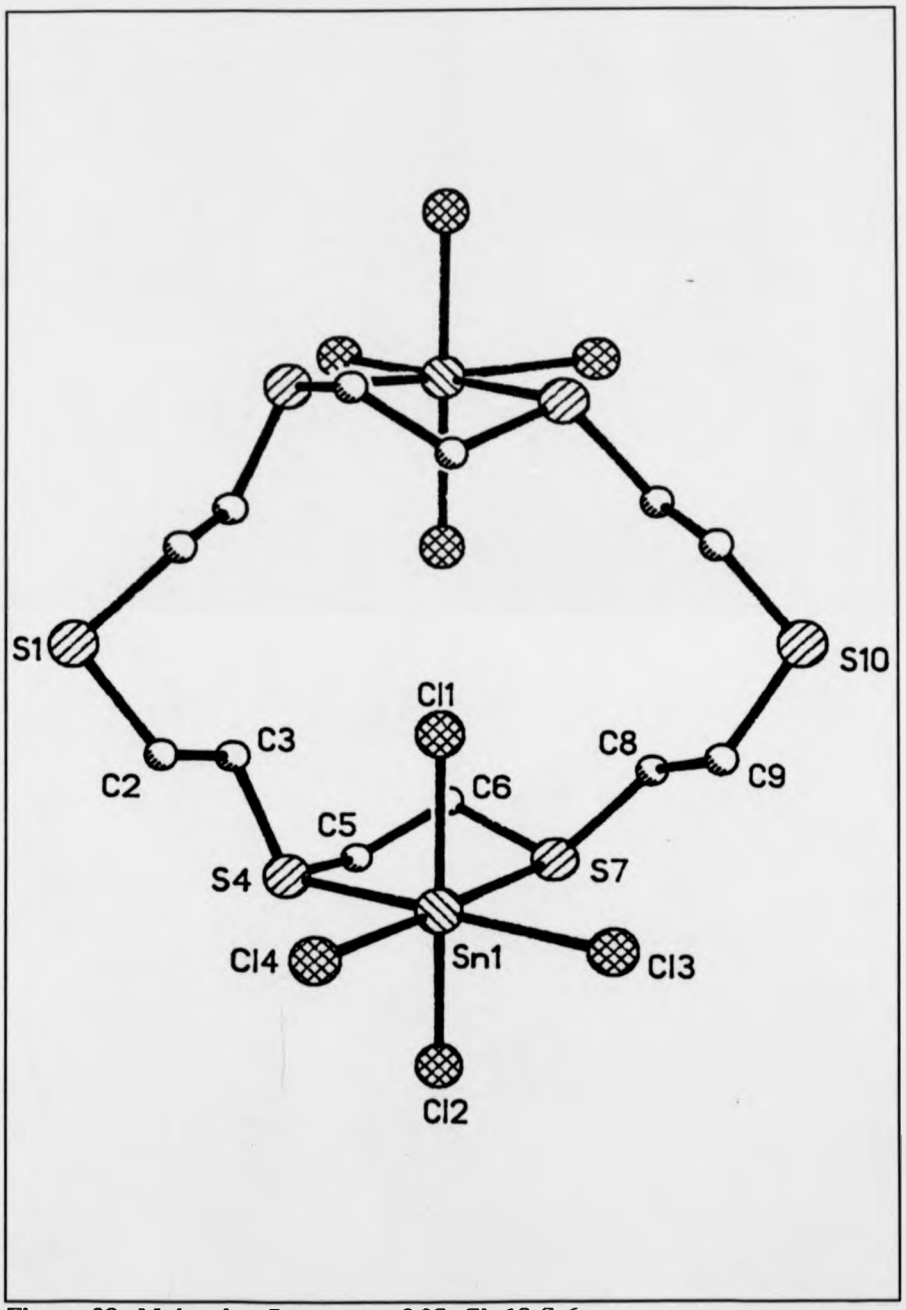


Figure 38. Molecular Structure of $2SnCl_4 \cdot 18\text{-}S\text{-}6$

A neutral binuclear adduct is revealed in which two separate $SnCl_4$ units are located at opposite ends of the cavity and on opposite sides of the ring plane. Each $SnCl_4$ unit achieves the favoured six coordination geometry via bidentate chelation to adjacent sulphur donors. However, there is slight deviation from a regular octahedron; S_4-Sn-S_7=83.8°, Cl_4-Sn-Cl_3=97.3°, Cl_3-Sn-S_4=169.4°, Cl_4-Sn-S_4=92.1°. Weak binding by the sulphur donor atoms is noted by comparison of the mean Sn-Cl and Sn-S, 2.37 Å *vs* 2.62 Å. The Sn-S bond lengths encountered in $2SnCl_4$·18-S-6 (mean 2.6181(2) Å) bear a close resemblance to those in compound $[SnCl_3(9\text{-}S\text{-}3)]_2[SbCl_6]$ (mean 2.637(4) Å) and other octahedral $SnCl_4$ compounds, *eg*. $SnCl_4(L)_2$, L= 1,5-DTCO, Sn-S 2.602(1) Å.[60]

This transannular arrangement has previously been reported for the complex $2SbCl_3$·18-S-6 which features terdentate attachment to each individual $SbCl_3$ moiety.[189]

IR Data

The IR spectrum of the product displays six bands in the far IR region, 443m, 340sh, 330sh, 321vs, 272s, (br) and 251sh cm^{-1}. This is consistent with bidentate chelation of the tin centre by the 18-S-6 ligand. Such an arrangement requires two ν(Sn-S) bands and four ν(Sn-Cl) bands.

CHAPTER FIVE

MONOAZACROWN ETHERS

MONOAZACROWN ETHERS

Having encountered problems with the O-donor macrocycles (as described in Chapter 3) it was hoped that reaction of titanium tetrachloride with monoazacrowns would produce favourable complex formation. Our interest focused on three particular monoazacrown ethers, 1-aza-12-crown-4, 1-aza-15-crown-5 and 1-aza-18-crown-6. It was felt that the inclusion of a N-H grouping would perhaps facilitate favourable bonding with $TiCl_4$ via a covalent Ti-N linkage, following HCl expulsion. This in turn would promote further auxiliary bonding with the donor oxygen atoms of the monoazacrown. Such a reaction has two possible products:-

1. formation of a Ti-N bond in which the titanium remains remote from the adjacent oxygen donors, possibly preferring interaction with solvent molecules. (Figure 39)

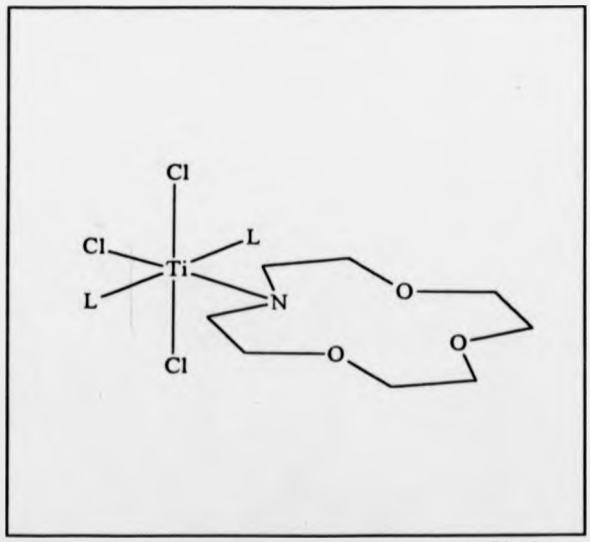


Figure 39. Partial Encapsulation of Ti(IV) by a Monoazacrown Ether

2. formation of a formal Ti-N bond may coerce the metal to interact with the remaining donor atoms leading to full encapsulation of the metal, as represented in Figure 40.

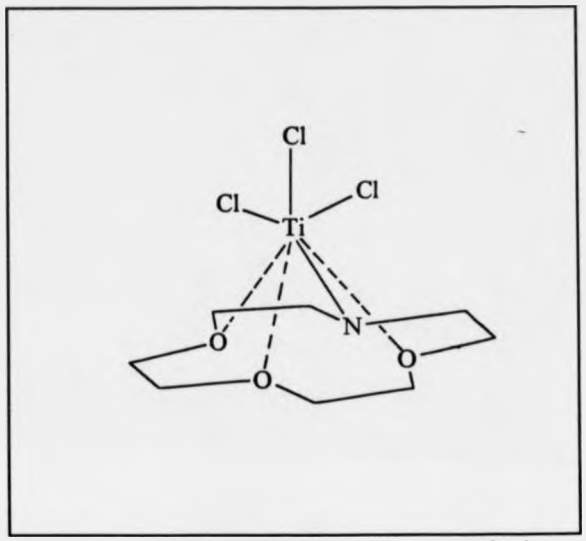


Figure 40. Full Encapsulation of Ti(IV) by a Monoazacrown Ether

RESULTS AND DISCUSSION

In each case equimolar addition of the desired ligand in MeCN to a solution of $TiCl_4$ in the same solvent yielded a semi-crystalline solid, with evolution of HCl. The gaseous evolution was not monitored. The reaction details are given in Table 50. Recrystallisation was hampered somewhat, as the products were insoluble in many solvents and only sparingly soluble in MeCN. The products were characterised using elemental analysis, IR and ^1H NMR spectroscopy. In this study the NMR spectra were recorded on a Bruker 400 MHz spectrometer. The microanalytical data for the initial products is given in Table 22.

Table 22. Microanalytical Data for the Initial Monoazacrown Products

Complex	C	H	N
	calc/obs (%)		
Product I [$TiCl_3$(1-aza-12-crown-4)]	29.25 28.79,	4.91 4.43,	4.26 3.98
Product II [$TiCl_3$(1-aza-15-crown-5)]	32.24 31.91,	5.41 5.09,	3.76 3.50
Product III [$TiCl_3$(1-aza-18-crown-6)]	34.60 34.17,	5.81 5.38,	3.36 2.96

The spectroscopic and microanalytical data for the initial products were consistent with the formation of complexes in which the titanium atoms are attached to the azacrown ethers through (Ti-N) bonds and interacts with some or all of the remaining donor atoms of the crown. The IR data for the initial products is given in Table 23 with that of the free ligands for comparison.

Table 23. Infrared Data for Free Ligands and Initial Products

Compound	IR (cm^{-1})
1-aza-12-crown-4	3306m, 1288m, 1216m, 1113s, 1027s, 937m, 910m, 784m, 590m, 554m
1-aza-15-crown-5	3242m, 1293m, 1253m, 1216m, 1125s, 1041m, 941m, 847m, 778m, 564m, 517m
1-aza-18-crown-6	3332m, 1288m, 1250m, 1212m, 1110s, 955m, 888m, 842w, 778w, 519w
[$TiCl_3$(1-aza-12-crown-4)] Product I	1284m, 1245m, 1150m, 1095s, 1032m, 960m, 935m, 850m, 825m, 335s, br
[$TiCl_3$(1-aza-15-crown-5)] Product II	1290m, 1230m, 1110m, 1095s, 958m, 845m, 345br, s
[$TiCl_3$(1-aza-18-crown-6)] Product III	1378m, 1301m, 1288s, 1245s, 1088vs, 945s, 849m, 839s, 321vs, br

Spectroscopic Analysis of the Initial Products

^{1}H NMR Data

a) Reaction with 1-aza-12-crown-4

The spectrum of the product contained four multiplets of equal intensity centred at δ 3.21, δ 3.58, δ 3.72 and δ 3.84 corresponding to the CH_2^a, CH_2^b, CH_2^c and CH_2^d protons respectively (Figure 41).

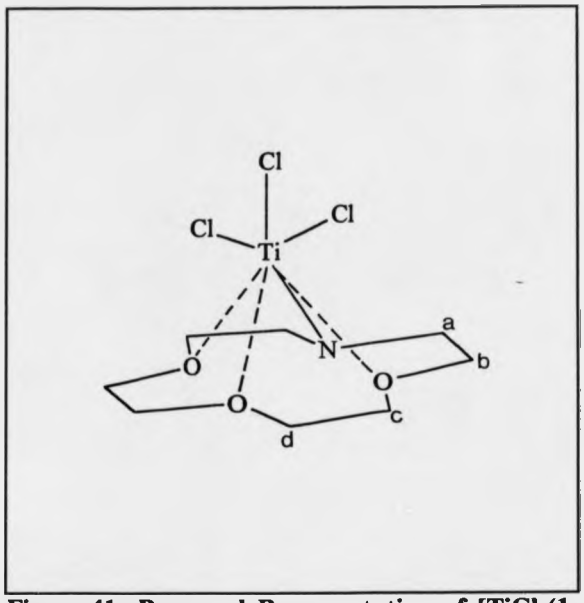


Figure 41. Proposed Representation of [$TiCl_3$(1-aza-12-crown-4)]

This is markedly different to the spectrum of the free ligand which displays three multiplets at δ 2.64, δ 3.50 and δ 3.53 of relative intensities 1:1:2. It appears the proton environment about each donor site is perturbed relative to that of the free ligand in accord with the proposed metal interactions.

b) Reaction with 1-aza-15-crown-5

The free ligand spectrum contains three signals: a singlet at δ 2.2 (N-H), a triplet δ 2.651 (CH_2^a) and a multiplet at δ 3.547 ($CH_2^{b,e}$) of relative intensities 1:4:16 respectively. Perturbation of the proton environment about each donor atom is reflected in the spectrum of the complex which displays signals at δ 3.160 (CH_2^a), δ 3.689 ($CH_2^{c,e}$), δ 3.848 (CH_2^b) of relative intensities 1:3:1 respectively in accord with the proposed metal interactions. (Figure 42)

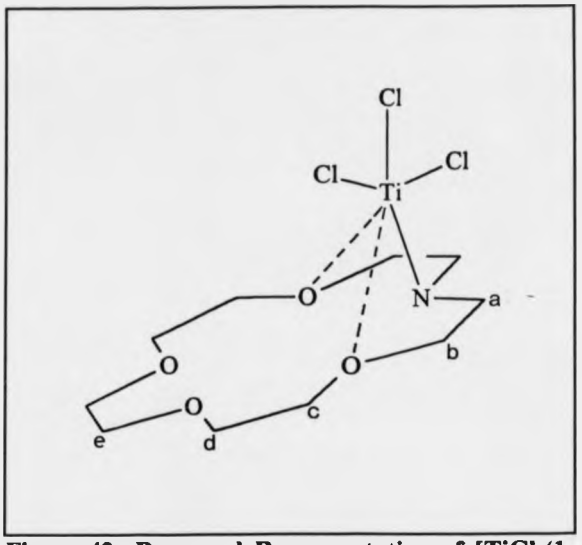


Figure 42. Proposed Representation of [$TiCl_3$(1-aza-15-crown-5)]

c) Reaction with 1-aza-18-crown-6

The spectrum of the product contains three multiplets centred at δ 3.14, δ 3.61 and δ 3.79 of relative intensities 1:4:1 corresponding to the protons CH_2^a, CH_2^{c-f} and CH_2^b respectively. In comparison with the free ligand [δ 2.68 (CH_2^a), δ 3.49 (CH_2^{c-f}) and δ 3.53 (CH_2^b)] each signal is shifted downfield as follows (Δ0.46), (Δ0.12) and (Δ0.27) respectively, in accord with the proposed metal/ligand interactions. (Figure 43)

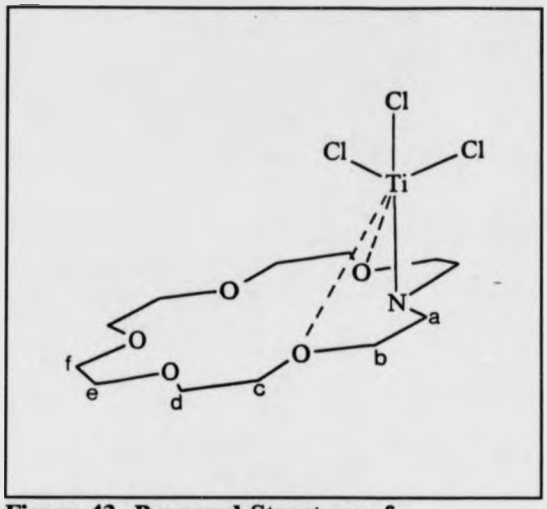


Figure 43. Proposed Structure of $[TiCl_3(1\text{-aza-18-crown-6})]$

IR Data

The IR evidence for each compound corroborates this picture whereby attachment of a $TiCl_3$ fragment to the ligand follows incipient HCl expulsion. The characteristic ν(Ti-Cl) frequency of the 1-aza-12-crown-4 compound is seen as an intense band at 340 cm^{-1}, whilst ν_{asym}(C-O-C) stretching band is shifted (Δ18 cm^{-1}) to a lower energy at 1095 cm^{-1}. For 1-aza-15-crown-5 a somewhat more pronounced shift (Δ30 cm^{-1}) of the ν_{asym} (C-O-C) band to lower energy at 1095cm^{-1} was noted. Similarly, the intense band at 340 cm^{-1} was assigned to ν(Ti-Cl). In the case of 1-aza-18-crown-6 compound the ν_{asym}(C-O-C) also undergoes a low energy shift (Δ22 cm^{-1}) to 1108 cm^{-1}. An intense ν(Ti-Cl) band is observed at 320cm^{-1}.

Spectroscopic Data for Recrystallised Monoazacrown Compounds

In an attempt to obtain pure crystalline samples of X-ray diffraction quality the initial samples were recrystallised by dissolving the compounds in MeCN and layering with dichloromethane. Substantial changes were noted in the ^{1}H NMR and IR spectra following recrystallisation. These observations were consistent with the presence of ν(N-H) and inclusion of water molecules in the compounds.

IR Data

The most noticeable difference was the appearance of an intense band at approximately 3100 cm^{-1} assigned to ν(N-H) stretching, suggesting reprotonation of the ligand. This was accompanied by a very broad shoulder trailing from the Nujol peak at 3000 cm^{-1}, assigned to ν(O-H) indicating H_2O or H_3O^+. The position and intensity of the ν(Ti-Cl) band was not affected. The findings are summarised in Table 24.

Table 24. IR Data for the Monoazacrown Products after Recrystallisation

Complex	ν(N-H) cm^{-1}	ν(C-O-C) cm^{-1}	$\Delta\nu$(C-O-C) cm^{-1}	ν(Ti-Cl) cm^{-1}
Product I'	3180	1080	10	340
Product II'	3160	1095	15	340
Product III'	3264	1106	4	320

^{1}H NMR Data

Close inspection of the ^{1}H NMR data revealed additional signals at δ 8.96 (1-aza-12-crown-4), δ 8.164 (1-aza-15-crown-5) and δ 7.417 (1-aza-18-crown-6) which were extremely broad and so difficult to integrate.

Previous studies from this laboratory have shown that the reaction system $SnCl_4$

and 1-aza-18-crown-6 yields the compound $[H_2L]_2[SnCl_5(H_2O)]_2 \cdot H_2O \cdot MeCN$, as confirmed by structural examination.[190] This reveals two separate $[H_2L]^+$ cations, (L = 1-aza-18-C-6), two aquapentachloro anions $[SnCl_5(H_2O)]^-$ and a molecule of water, which are linked by an extensive network of hydrogen bonding. It is presumed that the complex arises from the inadvertent partial hydrolysis of an initial product $[SnCl_3$(1-aza-18-C-6)]. The ^1H NMR spectrum for the latter compound contains three mutilpets centred at δ 3.24, 3.36 and 3.68 assigned to CH_2^a, $CH_2^{c\text{-}f}$ and CH_2^b which is consistent with partial encapsulation of the metal atom as shown in Figure 44.

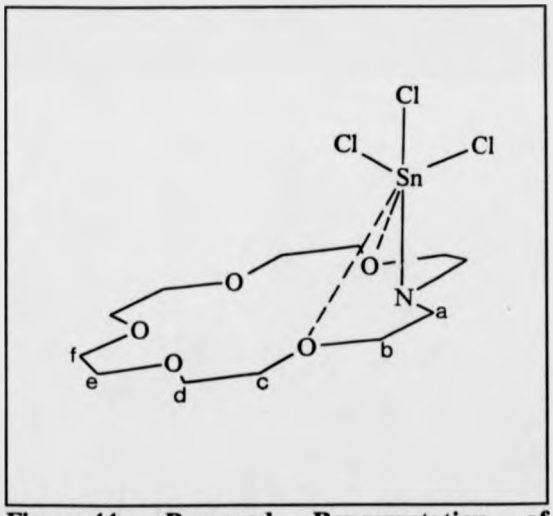


Figure 44. Proposed Representation of [$SnCl_3$(1-aza-18-C-6)]

In view of this and the spectroscopic evidence available for the $TiCl_4$ system, it is likely that $TiCl_4$ forms salts of a similar nature upon complexation with the monoazacrown ethers, L = 1-aza-12-C-4, 1-aza-15-C-5 and 1-aza-18-C-6. Again it is likely that similar hydrolysis products are obtained after recrystallisation.

This proposal gains further support from the microanalytical data. (Table 25)

Table 25. Microanalytical Data for the Recrystallised Monoazacrown Products

Compound	C H N calc/obs (%)
$[H_2L]_2[TiCl_5(H_2O)]_2 \cdot H_2O \cdot MeCN$ L = 1-aza-12-crown-4 Product I'	24.08 5.05 4.68 23.58 4.84 4.15
$[H_2L]_2[TiCl_5(H_2O)]_2 \cdot H_2O \cdot MeCN$ L = 1-aza-15-crown-5 Product II'	26.08 5.14 4.26 26.27 5.16 3.63
$[H_2L]_2[TiCl_5(H_2O)]_2 \cdot H_2O \cdot MeCN$ L = 1-aza-18-crown-6 Product III'	29.08 5.72 3.91 28.57 5.47 3.31

SUMMARY AND CONCLUSIONS

Crown Ethers

In spite of a favourable HSAB prediction, the reaction between crown ethers and the cation $[TiCl_3(MeCN)_3]^+$ does not always involve simple ligand exchange. Structural examination of $[\{TiCl(\mu\text{-}O)(12\text{-}C\text{-}4)\}_2][SbCl_6]_2$ and the formation of the analogous $[\{TiCl(\mu\text{-}O)(15\text{-}C\text{-}5)\}_2][SbCl_6]_2$ may be interpreted as either the product of a hydrolysis reaction or rupture of the crown ether.

Crown Thioethers

Spectroscopic evidence implies $TiCl_4$(9-S-3) most likely retains octahedral coordination through bidentate interaction of 9-S-3. Although this requires some degree of ligand reorganisation it appears more favourable than relinquishing a chloride ion from the metal centre upon coordination of the poor σ-donating ligand.

Although $SnCl_4$ and $TiCl_4$ are often chemically similar, the behaviour of $SnCl_4$ and 9-S-3 contrasts strongly with that of $TiCl_4$. The product $3SnCl_4 2$(9-S-3) contains the cation $[SnCl_3(9\text{-}S\text{-}3)]^+$ formed as a result of halide elimination. Despite the low σ-donating ability of 9-S-3, it appears that the favoured hexacoordination and preferred endodenticity of 9-S-3 act in concert to displace the chloride ion.

Monoazacrown Ethers

The most significant point which emerges from this study is that rupture of the monoazacrown ethers in the presence of $TiCl_4$ is not seen. This is probably due to the facile formation of the Ti-N bond.

CHAPTER SIX

CONTROLLED HYDROLYSIS REACTIONS OF SOLVATED $[TiCl_n]^{(4-n)+}$ SPECIES

CONTROLLED HYDROLYSIS REACTIONS OF SOLVATED $[TiCl_n]^{(4-n)+}$ SPECIES

INTRODUCTION

It is not surprising to find a wealth of reports covering the chemistry of titanoxanes considering the degree of Lewis acid character and high oxophilicity of titanium. Such species contain either the terminal Ti=O titanyl unit or oxo-bridges. Examples of the former are rare, due to the reactivity of the Ti=O bond, with only a few examples known:-

$[Et_4N]_2[Ti(O)Cl_4]$,[191] [Ti(O)(OEP)] OEP = 2,3,7,8,12,13,17,18-octaethylporphinato dianion,[192]

[TiO(OEPMe$_2$)] OEPMe$_2$ = α-γ-dimethyl-α-γ-dihydrooctaethylporphinato dianion,[193]

[Ti(O)(PC)] PC = $(C_{32}H_{16}N_8)^{2-}$ the phthalcyaninato dianion[194]

and more recently

Ti(O)(tmtaa) (H_2tmtaa = 6,8,15,17-tetramethyl-5,14-dihydro-5,9,14,18-tetraazadibenzo[a,h]cyclotetradecene[195,196,151]

The instability and reactivity associated with the titanyl unit can often be used to great effect. The TiO^{2+} units have a tendency to participate in oxo-bridging interactions with oxophilic metal centres of other compounds providing a route to μ-heteronuclear dimeric compounds. This is exemplified by [Ti(O)(tmtaa)] which yields a series of heterobinuclear μ-oxo-bridged dimers following reaction with the oxophilic metal salen complexes of Fe(II), Cr(III), Mn(II), V(III), Sn(IV) and Mo(IV), (Salen=salicyclaldimine(ethylenediamine).[195] As a result of this

study the complex $[(tmtaa)Ti(\mu\text{-}O)_2(Si(CH_3)_3)]_2$ was structurally characterised. The tmtaa ligand appears to offers some steric control, limiting further hydrolysis. Studies of the oxo-bridged titanoxanes display a tremendous bias towards species containing bulky ligands such as Cp, in $[(Cp_2TiCl)_2O]$,[197] and macrocyclic entities, *eg.* 9-N-3, in $[Ti_4(9\text{-}N\text{-}3)_4(\mu\text{-}O)_6]Br{\cdot}4H_2O$.[198]

In all these hydrolysis reactions it is apparent that the outcome is dependent upon the Ti/H_2O stoichiometry and the conditions employed. In the case of Cp^* systems, this is typified by the work of Royo *et al.*[164] Controlled hydrolysis of Cp^*TiX_3 (X = Cl, Br or I) in the presence of the base $NHEt_2$ yields a variety of products depending on the molar ratio of $Ti:H_2O$. Use of a molar ratio of 2:1, $Cp^*TiX_3:H_2O$, affords dimers of the type $[(Cp^*TiX_2)_2(\mu\text{-}O)]$. The rate of formation is dominated by steric factors as the large bulkier iodide appears to hinder the attack of the water molecule at the titanium centre. This is at odds with bond strength and degree of covalent character of the Ti-X bonds. Initial results suggested a further decrease in the rate of hydrolysis when the molar ratio is lowered to 1:1. This reaction was not pursued although Cp^*TiCl_3 and Cp^*TiBr_3 yield $[Cp^*TiCl(\mu\text{-}O)]_3$ and $[Cp^*TiBr(\mu\text{-}O)]_4$ respectively. Removal of all three halogen atoms yields $(Cp^*Ti)_4(\mu\text{-}O)_6$ via the use of a molar ratio of 3:2 Ti/H_2O.

RESULTS AND DISCUSSION

The intriguing results obtained in 1963 by Feltz,[199] following a study of simple oxo titanium species, prompted our investigation in this area of chemistry. The work of Feltz provided the compounds $Ti_2Cl_6O{\cdot}4MeCN$ and $Ti_2Cl_6O{\cdot}6.5MeCN$ following partial hydrolysis of $TiCl_4(MeCN)_2$ in MeCN. Furthermore the analogous reaction between $Ti_2Cl_6O{\cdot}4MeCN$ and dioxane yielded an adduct which agrees with the formulation $Cl_3Ti\text{-}O\text{-}TiCl_3{\cdot}4(dioxane)$. This study provided the impetus for our examination of simple chloro-titanium(IV) species $[TiCl_n]^{(4-n)+}$, using $TiCl_4(MeCN)_2$, as a repeat of the Feltz study (n=4), and the solvated pentachloroanion $[TiCl_5(MeCN)]^-$ where n=5.

Controlled hydrolysis of the appropriate species in MeCN was achieved by syringe addition of the correct amount of a standard H_2O/MeCN solution, ($0.0406gH_2O/cm^3$). The standard solution was prepared by addition of H_2O (2.030g) to MeCN in a volumetric flask (50 cm^3).

Complete characterisation of the products was achieved using microanalysis, IR spectroscopy and X-ray structural examination. The microanalytical and X-ray data is listed in Tables 26, 27 and 28 respectively.

Microanalytical Data

The data obtained is listed in Table 26 and is consistent with the proposed formulations in each case.

Table 26. Microanalytical Data For the Controlled Hydrolysis Products

Compound	C H N Cl calc/obs (%)
$[Mg(MeCN)_6][Ti_2Cl_8(O)(MeCN)_2]\cdot 4MeCN$	31.59, 3.98, 18.42, 31.87 31.39, 3.78, 18.22, 29.94
$[TiCl_2(MeCN)_2(\mu\text{-}O)]_4\cdot 2MeCN$	25.30, 3.18, 14.75, 29.87 24.98, 3.00, 14.29, 29.66

$[Mg(MeCN)_6][\{TiCl_4(MeCN)\}_2(\mu\text{-}O)]$

Sobota *et al*[123] have shown that reaction of $MgCl_2$ and $TiCl_4$ in a 1:2 molar ratio provides $[Mg(THF)_6][TiCl_5(THF)]_2$ from THF solution. Through the use of MeCN solvent this was seen as a likely route to the desired pentachloro titanium anion $[TiCl_5(MeCN)]^-$ with subsequent controlled hydrolysis providing the title compound. (Eqn 25)

$$MgCl_2 + 2TiCl_4 \rightarrow [Mg(MeCN)_6][TiCl_5(MeCN)]_2 \xrightarrow{H_2O} [Mg(MeCN)_6][Ti_2Cl_8(O)(MeCN)_2] + 2HCl \quad (25)$$

This hydrolysis affords the title compound as yellow air/moisture sensitive crystals and is seen to involve exchange of MeCN for H_2O with HCl elimination.

IR Data

The IR spectrum contains a doublet at 2313, 2286 cm^{-1} characteristic of coordinated MeCN. The broad band at 345 cm^{-1} is assigned to ν(Ti-Cl) but most likely incorporates a contribution from the Mg-N stretching mode which is seen at 330 cm^{-1} in $[Mg(MeCN)_6]^{2+}$ (ν_{14}).[200] More importantly the strong band at 786cm^{-1} ν_{asym}(Ti-O-Ti) is indicative of a linear μ-oxo linkage between two titanium groups.

X-Ray Crystallography

In order to prevent hydrolysis during X-ray examination, suitable crystals were mounted in Lindemann capillary tubes. The molecular structure of $[Mg(MeCN)_6][\{TiCl_4(MeCN)\}_2(\mu\text{-}O)]$ is shown in Figure 45, revealing a discrete $[Mg(MeCN)_6]^{2+}$ cation, a $[\{TiCl_4(MeCN)\}_2(\mu\text{-}O)]^{2-}$ anion and four MeCN molecules. Selected bond distances and angles are given in Table 27. The cation is unexceptional and has the expected bond dimensions[186] with Mg-N bond distances ranging from 2.129(6) to 2.184(7) Å (Table 58). The anion is the main point of interest and is shown in Figure 46 with relevant atom labelling. Each titanium centre has near octahedral geometry, being bonded to four chlorine atoms in an equatorial plane with mutually *trans* MeCN ligands and bridging oxygen atom. The eclipsed conformation results in D_{4h} symmetry. Bond angles about the *trans* ligands display only marginal deviation from linearity;

	N_{11}-Ti_1-O	178.5°
	Ti_1-O-Ti_2	174.7°
and	O-Ti_2-N_{21}	177.0°

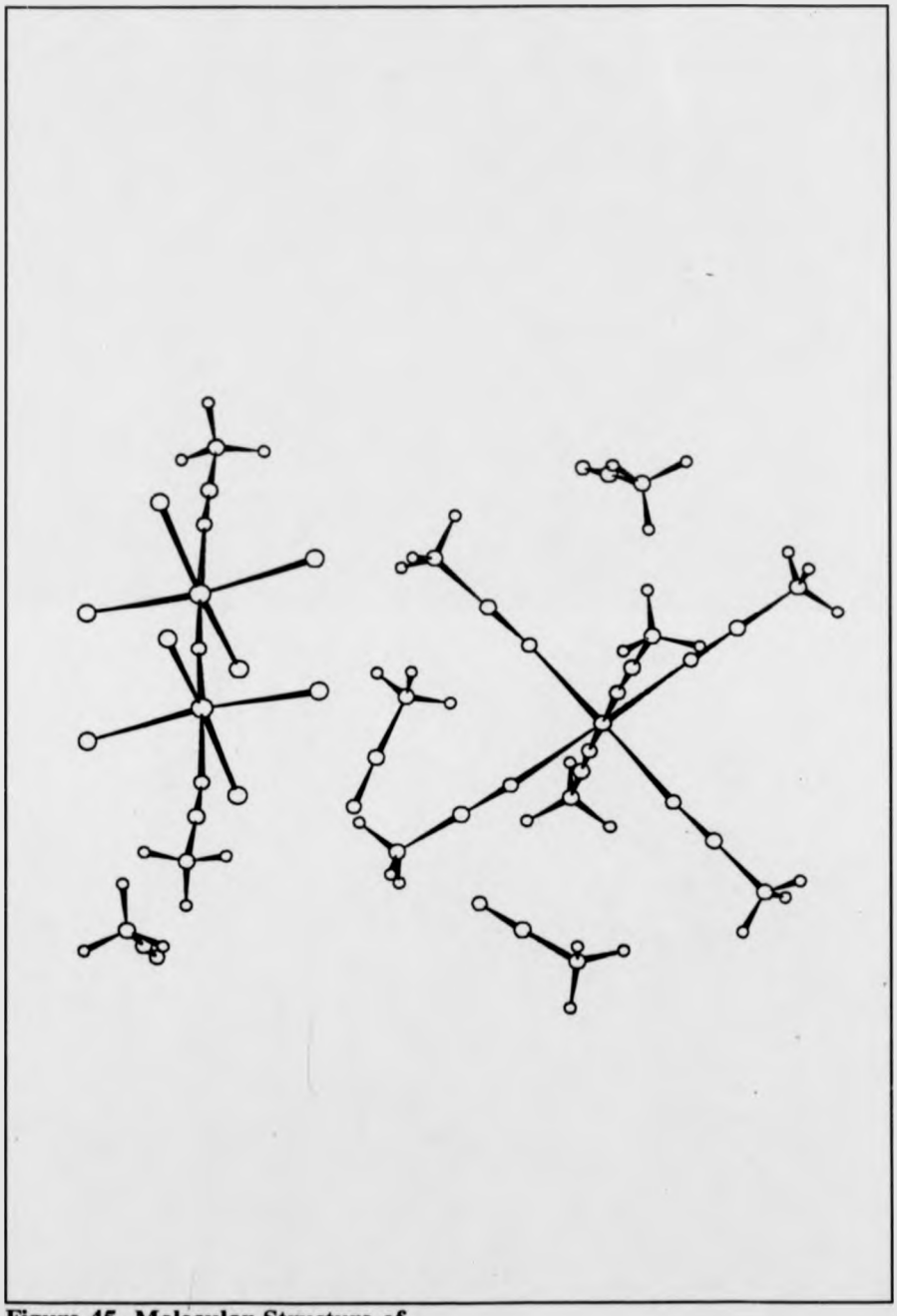


Figure 45. Molecular Structure of $[Mg(MeCN)_6][\{TiCl_4(MeCN)\}_2(\mu\text{-}O)]\cdot 4MeCN$

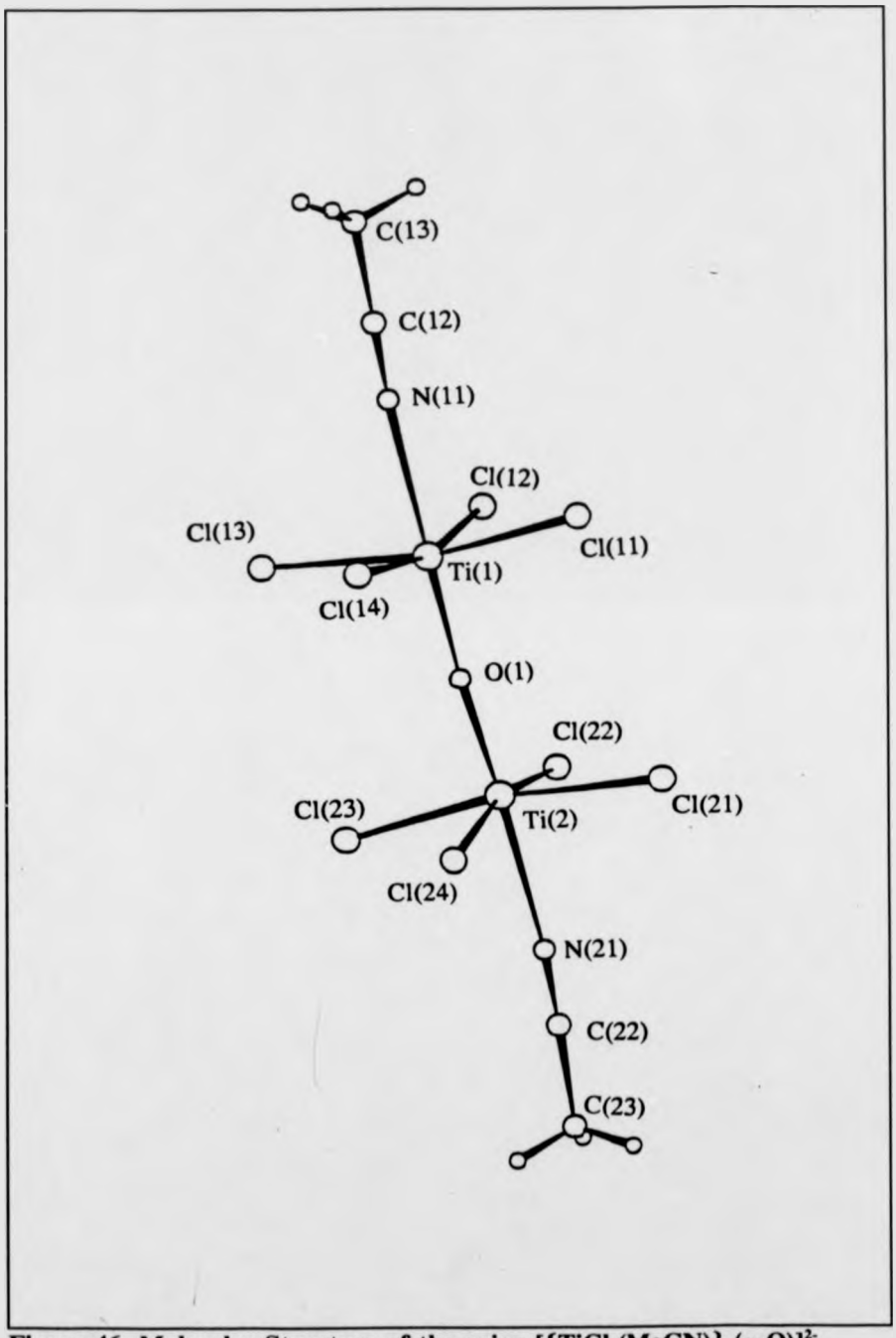


Figure 46. Molecular Structure of the anion $[\{TiCl_4(MeCN)\}_2(\mu\text{-}O)]^{2-}$

Table 27. Selected Bond Lengths (Å) and Angles (°) for $[Mg(MeCN)_4][\{TiCl_4(MeCN)\}_2(\mu\text{-}O)]$

Ti(1)-O(1)	1.783(4)
Ti(1)-N(11)	2.273(5)
Ti(1)-Cl(11)	2.316(2)
Ti(1)-Cl(12)	2.296(2)
Ti(1)-Cl(13)	2.318(2)
Ti(1)-Cl(14)	2.323(2)
Ti(2)-O(1)	1.764(4)
Ti(2)-N(21)	2.278(5)
Ti(2)-Cl(21)	2.314(2)
Ti(2)-Cl(22)	2.306(2)
Ti(2)-Cl(23)	2.318(2)
Ti(2)-Cl(24)	2.316(2)
O(1)-Ti(1)-N(11)	178.5(2)
O(1)-Ti(1)-Cl(12)	95.08(14)
N(11)-Ti(1)-Cl(12)	83.7(2)
O(1)-Ti(1)-Cl(11)	95.54(13)
N(11)-Ti(1)-Cl(11)	83.54(14)
Cl(12)-Ti(1)-Cl(11)	90.93(8)
O(1)-Ti(1)-Cl(13)	96.00(14)
N(11)-Ti(1)-Cl(13)	84.95(14)
Cl(12)-Ti(1)-Cl(13)	89.17(7)

Cl(11)-Ti(1)-Cl(13)	168.41(8)
O(1)-Ti(1)-Cl(14)	97.2(2)
N(11)-Ti(1)-Cl(14)	84.0(2)
Cl(12)-Ti(1)-Cl(14)	167.62(9)
Cl(11)-Ti(1)-Cl(14)	89.18(7)
Cl(13)-Ti(1)-Cl(14)	88.25(7)
O(1)-Ti(2)-N(21)	177.0(2)
O(1)-Ti(2)-Cl(22)	98.1(2)
N(21)-Ti(2)-Cl(22)	84.5(2)
O(1)-Ti(2)-Cl(21)	96.43(14)
N(21)-Ti(2)-Cl(21)	85.0(2)
Cl(22)-Ti(2)-Cl(21)	89.62(7)
O(1)-Ti(2)-Cl(24)	95.3(2)
N(21)-Ti(2)-Cl(24)	82.0(2)
Cl(22)-Ti(2)-Cl(24)	166.54(9)
Cl(21)-Ti(2)-Cl(24)	89.19(7)
O(1)-Ti(2)-Cl(23)	95.19(14)
N(21)-Ti(2)-Cl(23)	83.4(2)
Cl(22)-Ti(2)-Cl(23)	89.08(7)
Cl(21)-Ti(2)-Cl(23)	168.37(8)
Cl(24)-Ti(2)-Cl(23)	89.40(8)
Ti(2)-O(1)-Ti(1)	174.7(3)

The chlorine atoms around each titanium atom are virtually eclipsed with Cl-Ti···Ti-Cl torsion angles of less than 2°. This implies there is minimal steric repulsion between the chlorine atoms. The two Ti-O bond dimensions are closely related at 1.783(4)/1.764(4) Å. Similarly the Ti-N distances are approximately equivalent at 2.273(5) and 2.278(5) Å. These dimensions bear a close resemblance to those found in the isomeric form isolated from the reaction system $TiCl_4/Se(SiMe_3)_2/PPh_4Cl$ following inadvertent hydrolysis.[201] In this latter case the MeCN ligand occupies a *cis* location with respect to the bridging oxygen atom.

$[TiCl_2(MeCN)_2(\mu\text{-}O)]_4$

The title compound was obtained from controlled hydrolysis of $TiCl_4$ (1 mol), as the *bis* adduct $TiCl_4(MeCN)_2$ formed *in situ*. In order to induce crystal growth it was necessary to maintain the solution at -5°C for several days. Following this, pale yellow needle crystal deposited. The first indication of hydrolysis was confirmed by the band at 792 cm^{-1}, ν_{asym}(Ti-O-Ti), assigned to a linear Ti-O-Ti linkage. A characteristic ν(CN) doublet for coordinated MeCN was observed at 2308, 2280 cm^{-1} and a ν(Ti-Cl) band at 382 cm^{-1}.

X-Ray Crystallography

The molecular configuration of $[TiCl_2(MeCN)_2(\mu\text{-}O)]_4$, as illustrated in Figure 47, with atom labelling, consists of four $[TiCl_2(MeCN)_2]$ units linked by four oxo-bridges to produce an eight-membered ring of alternating Ti and O atoms. The bond angles and bond lengths are given in Table 28.

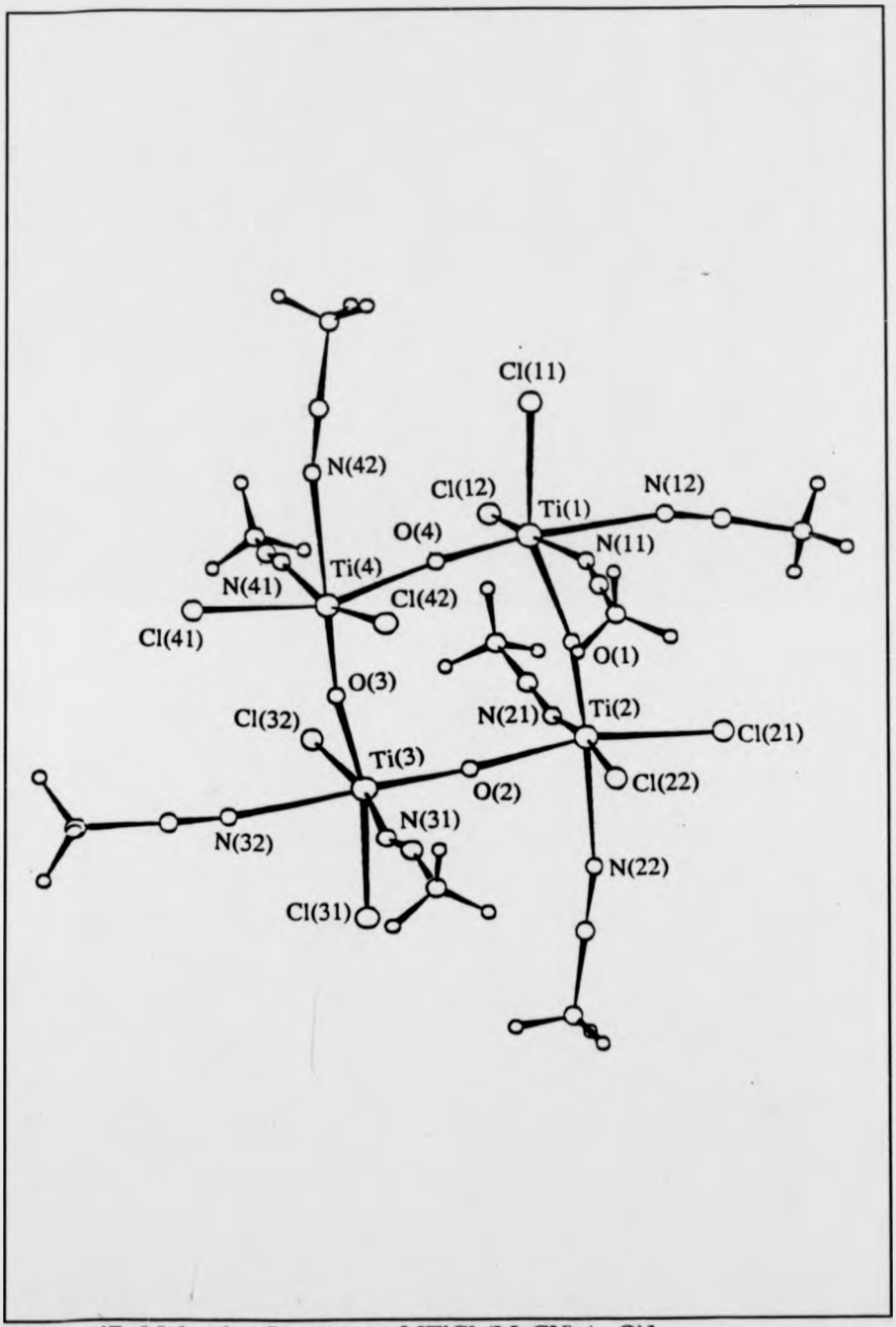


Figure 47. Molecular Structure of $[TiCl_2(MeCN)_2(\mu\text{-}O)]_4$

Table 28. Selected Bond Lengths (Å) and Angles (°) for $[TiCl_2(MeCN)_2(\mu\text{-}O)]_4$

Ti(1)-O(4)	1.664(10)
Ti(1)-O(1)	1.936(10)
Ti(1)-N(11)	2.166(14)
Ti(1)-Cl(12)	2.287(5)
Ti(1)-Cl(11)	2.323(4)
Ti(1)-N(12)	2.356(13)
Ti(2)-O(1)	1.683(10)
Ti(2)-O(2)	1.960(10)
Ti(2)-N(21)	2.168(12)
Ti(2)-N(22)	2.305(12)
Ti(2)-Cl(22)	2.295(5)
Ti(2)-Cl(21)	2.329(4)
Ti(3)-O(2)	1.672(10)
Ti(3)-O(3)	1.967(9)
Ti(3)-N(31)	2.207(13)
Ti(3)-Cl(32)	2.285(4)
Ti(3)-N(32)	2.314(14)
Ti(3)-Cl(31)	2.341(4)
Ti(4)-O(3)	1.653(9)
Ti(4)-O(4)	1.954(10)
Ti(4)-N(41)	2.191(14)
Ti(4)-Cl(42)	2.280(5)

Ti(4)-Cl(41)	2.334(4)
Ti(4)-N(42)	2.336(12)
O(4)-Ti(1)-O(1)	97.6(4)
O(4)-Ti(1)-N(11)	89.3(5)
O(1)-Ti(1)-N(11)	80.1(5)
O(4)-Ti(1)-Cl(12)	99.9(4)
O(1)-Ti(1)-Cl(12)	94.5(4)
N(11)-Ti(1)-Cl(12)	170.0(4)
O(4)-Ti(1)-Cl(11)	99.2(3)
O(1)-Ti(1)-Cl(11)	158.6(3)
N(11)-Ti(1)-Cl(11)	87.0(4)
Cl(12)-Ti(1)-Cl(11)	95.5(2)
O(4)-Ti(1)-N(12)	171.2(5)
O(1)-Ti(1)-N(12)	78.2(4)
N(11)-Ti(1)-N(12)	82.3(5)
Cl(12)-Ti(1)-N(12)	88.3(4)
Cl(11)-Ti(1)-N(12)	83.2(4)
O(1)-Ti(2)-O(2)	97.9(4)
O(1)-Ti(2)-N-(21)	92.0(5)
O(2)-Ti(2)-N(21)	82.5(4)
O(1)-Ti(2)-N(22)	172.0(5)
O(2)-Ti(2)-N(22)	79.7(4)
N(22)-Ti(2)-N(21)	80.1(5)
O(1)-Ti(2)-Cl(22)	100.5(4)

O(2)-Ti(2)-Cl(22)	94.1(3)
N(21)-Ti(2)-Cl(22)	167.4(4)
N(22)-Ti(2)-Cl(22)	87.3(4)
O(1)-Ti(2)-Cl(21)	96.5(3)
O(2)-Ti(2)-Cl(21)	161.6(3)
N(21)-Ti(2)-Cl(21)	85.7(4)
N(22)-Ti(2)-Cl(21)	84.5(3)
Cl(22)-Ti(2)-Cl(21)	94.4(2)
O(2)-Ti(3)-O(3)	97.8(4)
O(2)-Ti(3)-N(31)	90.2(5)
O(3)-Ti(3)-N(31)	82.0(4)
O(2)-Ti(3)-Cl(32)	101.3(4)
O(3)-Ti(3)-Cl(32)	91.9(3)
N(31)-Ti(3)-Cl(32)	167.6(4)
O(2)-Ti(3)-N(32)	169.1(5)
O(3)-Ti(3)-N(32)	78.5(4)
N(31)-Ti(3)-N(32)	79.2(5)
Cl(32)-Ti(3)-N(32)	89.1(4)
O(2)-Ti(3)-Cl(31)	98.8(3)
O(3)-Ti(3)-Cl(31)	160.3(3)
N(31)-Ti(3)-Cl(31)	87.4(3)
Cl(32)-Ti(3)-Cl(31)	95.1(2)
N(32)-Ti(3)-Cl(31)	83.3(4)
O(4)-Ti(4)-O(3)	98.2(4)

O(3)-Ti(4)-N(41)	89.8(5)
O(4)-Ti(4)-N(41)	81.5(4)
O(3)-Ti(4)-Cl(42)	99.1(4)
O(4)-Ti(4)-Cl(42)	94.2(3)
N(41)-Ti(4)-Cl(42)	170.6(4)
O(3)-Ti(4)-Cl(41)	98.9(3)
O(4)-Ti(4)-Cl(41)	158.9(3)
N(41)-Ti(4)-Cl(41)	86.2(3)
Cl(42)-Ti(4)-Cl(41)	95.3(2)
O(3)-Ti(4)-N(42)	172.4(5)
O(4)-Ti(4)-N(42)	77.4(4)
N(41)-Ti(4)-N(42)	83.4(5)
Cl(42)-Ti(4)-N(42)	87.5(4)
Cl(41)-Ti(4)-N(42)	84.2(3)
Ti(2)-O(1)-Ti(1)	172.3(5)
Ti(3)-O(2)-Ti(2)	166.8(6)
Ti(4)-O(3)-Ti(3)	72.6(5)
Ti(1)-O(4)-Ti(4)	168.5(6)

The $[Ti(\mu\text{-}O)]_4$ ring deviates substantially from planarity, with four titanium atoms *ca* 0.28 Å alternately above and below the plane defined by the four oxygen atoms, planar to within 0.06 Å. A slight deviation from linearity is observed for the four Ti-O-Ti angles which range from 166.8(6) to 172.6(5)°. The near octahedral and equivalent geometry about each titanium atom comprises two mutually *cis* terminal chlorine atoms, two mutually *cis* MeCN ligands and two mutually *cis* bridging oxygen atoms.

In this case the Ti-O bonds are atypical in that they are not equivalent, differing somewhat with respect to the nature of the *trans* ligand. Those bonds *trans* to MeCN (mean value 1.668 Å) are shorter than those *trans* to a chlorine atom (mean value 1.954 Å). The Ti-N bond distance *trans* to the shorter Ti-O bonds are longer *ca* 2.320 Å compared to those *trans* to the chlorine atoms *ca* 2.184 Å. A similar pattern emerges for the Ti-Cl distances with those *trans* to oxygen being significantly longer (2.323(4), 2.329(4), 2.341(4) and 2.334(4) Å) than those *trans* to the MeCN ligand (2.287(5), 2.295(5), 2.285(4) and 2.80(5)Å)

Other tetrameric titanoxanes are known containing a Ti_4O_4 core unit *viz*;

Compound	Core Unit
$[(\eta^5\text{-}Cp)TiCl(\mu\text{-}O)]_4$	planar[202]
$[(\eta^5\text{-}Cp)Ti(OC_9H_{11})(\mu\text{-}O)]_4$	planar[203]
$[(\eta^5\text{-}C_5HMe_4)TiBr(\mu\text{-}O)]_4$	planar[204]
$[(\eta^5\text{-}C_5H_4)(SiMe_3))Ti(NCS)(\mu\text{-}O)]_4$	planar[205]
$[(TiCl)_2(\mu_2\text{-}O)\{\mu_2\text{-}\eta^5\text{-}\eta^5\text{-}(C_5H_4)_2SiMe_2\}]_2(\mu_2\text{-}O)_2$	non-planar[206]
$[(\eta^5\text{-}C_5H_4Me)TiCl(\mu\text{-}O)]_4$	planar[207]

It is important to note that the examples listed above all contain metal atoms with

four coordinate (tetrahedral) geometries. The compound isolated in this study represents the first example of a Ti_4O_4 skeletal unit in which the metal centre is octahedrally coordinated.

A closely related hydrolysis product of $TiCl_4$ contains the cubic octameric titanium cation $[Ti_8O_{12}(H_2O)_{24}]^{8+}$ in which each octahedral metal centre is bonded to three water molecules and three separate bridging oxygen atoms, (Ti-O (mean) 1.820 (1.791(2) - 1.859(2) Å, Ti-O-Ti (mean) 154.6° (153.10(11) - 156.03(11)°).[208]

It is clear that, the Feltz[199] compound $[(MeCN)_2Cl_3Ti\text{-}O\text{-}TiCl_3(MeCN)_2]$ was not isolated from this present study, rather it is the hydrolysed dimer. (Figure 48)

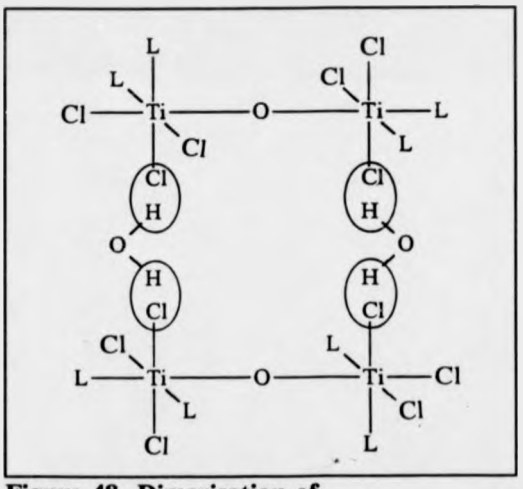


Figure 48. Dimerisation of $[(MeCN)_2Cl_3Ti\text{-}O\text{-}TiCl_3(MeCN)_2]$

Yet, further hydrolysis (dimerisation) could lead to a cubic octameric derivative $[Ti_8O_{12}(MeCN)_{16}Cl_8]$ in which the titanium atoms occupy the corner positions of the cube and are coordinated to two MeCN molecules, one chlorine atom and three separate bridging oxygen atoms. Such a compound could be considered as

a direct analogue to the cubic octamer $[Ti_8O_{12}(H_2O)_{24}]^{8+}$.[208]

Provided a 2:1 molar ratio is strictly obeyed, it is possible to envisage the formation of a series of dititanoxane species through controlled hydrolysis of octahedral, solvated chloro-titanium(IV) compounds according to Equation 26.

$$2[TiCl_nL_{6-n}]^{(4-n)+} + H_2O \xrightarrow{L} [\{TiCl_{n-1}L_{6-n}\}_2(\mu\text{-}O)]^{(8-2n)+} + 2HCl \qquad (26)$$

It is noteworthy that, allowing for the variant nature of the ligands coordinated to the titanium atom of these titanoxanes there appears to be no obvious correlation between Ti-O bond distances in the T-O-Ti linkages despite a change in electronic charge *viz*; (Table 29)

Table 29. Correlation of Bond Length and Charge in Selected Titanoxanes

Compound	Charge	Ti-O (Å)	Ref
$[\{TiCl_4(MeCN)\}_2(\mu\text{-}O)]^{2-}$	-2	1.804	201
$[\{TiCl_4(MeCN)\}_2(\mu\text{-}O)]^{2-}$	-2	1.774	This work
$[\{TiCl_3(THF)_2\}_2(\mu\text{-}O)]$	0	1.787	209
$[TiCl_2(MeCN)_2(\mu\text{-}O)]_4$	0	1.668, 1.954	This work
$[\{Ti(tmtaa)\}_2(\mu\text{-}O)]^{2+}$	+2	1.806, 1.830	196
$[\{(\eta^5\text{-}C_5H_5)_2Ti(H_2O)\}_2(\mu\text{-}O)]^{2+}$	+2	1.829	210

However, there is a distinct reduction of 0.2 Å in the Ti=O linkages, as a result of the increased multiple bond character in the latter *viz*, [Ti(O)(tmtaa)] Ti=O 1.653 Å[195] and [Ti(O)(OEP)][192] Ti=O 1.613 Å, OEP=2,3,7,8,12,13,17,17-octathylporphinto dianion.

CHAPTER SEVEN

REACTIONS OF SUBSTITUTED CYCLOPENTADIENYL TITANIUM TRICHLORIDES WITH CARBOXYLIC ACIDS

REACTIONS OF SUBSTITUTED CYCLOPENTADIENYL TITANIUM TRICHLORIDE WITH CARBOXYLIC ACIDS

During a period of my Ph.D studies I was able to participate in an exchange programme involving the Department of Chemistry at the University of Acalá de Henares, Madrid. The research was funded by the British Council and carried out under the direction of Professor Royo of the above University and Professor Wallbridge and Dr Willey of the University of Warwick. The work involved a study of the reactions of substituted cyclopentadienyl titanium species with the carboxylic acid, *p*-toluic acid.

INTRODUCTION

The following discussion is intended as a brief summary of the work of Professor Royo *et al*. This work concerns the isolation of electron deficient organotitanium complexes of potential Ziegler-Natta catalytic ability. Most of his work has concentrated on the synthesis of cyclopentadienyl Group 4 complexes.[211] Of particular interest is the series of compounds prepared from pentamethylcyclopentadienyl titanium trichloride, (henceforth Cp^*TiCl_3). Early synthetic procedures did not provide Cp^*TiCl_3 in quantities sufficient for a systematic study.[212, 213] Royo *et al*[214] devised an efficient one-step method based on the reaction shown in Equation 27.

$$Cp^*SiMe_3 + TiCl_4 \rightarrow Cp^*TiCl_3 + Me_3SiCl \qquad (27)$$

Alkylated derivatives of Cp^*TiCl_3 can be readily prepared and careful control of

the stoichiometry permitted the isolation of partially or fully alkylated derivatives. The use of Grignard or organolithium reagents led to the successful isolation of a series of di- and tri-alkylated derivatives.[215] Examples of which include:-

$$Cp^*TiCl_3 + Mg(CH_2Ph)_2(THF)_2 \rightarrow Cp^*TiCl(CH_2Ph_2)_2 + MgCl_2 + 2THF \quad (28)$$

and

$$Cp^*TiCl_3 + 3LiR \rightarrow Cp^*TiR_3 + 3LiCl \quad (29)$$

R = CH_2SiMe_3

R = C_6F_5

R = Me

These Cp^*Ti compounds are particularly interesting as they exhibit a higher thermal stability in comparison to the Cp derivatives, *eg*. $CpTiMe_3$ decomposes at 20°C whereas Cp^*TiMe_3 melts at 75-76°C without decomposition. Such stability is striking bearing in mind the compounds are formally only twelve electron species.

Having developed an efficient procedure for isolating $CpTiCl_3$ and the methyl derivative Cp^*TiMe_3 Royo *et al* set about studying the derivative chemistry, with a view to isolating eighteen electron complexes. As a route to isolating these complexes, carboxylic acids were introduced as potential bidentate chelating donors.[215] The use of three equivalents of acid brings about displacement of all three methyl groups from Cp^*TiMe_3 with concomitant release of methane. (Eqn 30.)

$$Cp^*TiMe_3 + 3HO_2CR \rightarrow Cp^*Ti(O_2CR)_3 + 3CH_4 \quad (30)$$

where R = Me, Ph and *p*-$MeOC_6H_4$

The carboxylates show a higher resistance to hydrolysis than the parent titanium compound. It was hoped that lowering the molar ratio to 1:2 or 1:1 would result in the formation of bis and mono carboxylates according to Equation 31.

$$Cp^*TiMe_3 + nHO_2CR \rightarrow Cp^*Ti\text{-}Me_{3-n}(O_2CR)_n + nCH_4 \qquad (31)$$
$$n = 2$$
$$n = 1$$

However an inseparable mixture of mono, bis and tris-carboxylates and some starting material is always produced.

Surprisingly, under direct sunlight the reaction shown in Equation 31 affords dimeric titanium(III) carboxylates of composition $[\{Cp^*Ti(O_2CR)_2\}_2]$, where R = Me, Ph and *p*-$MeOC_6H_4$. Structural examination revealed the four carboxylate groups bridge both titanium centres. This arrangement can be seen in Figure 49 which depicts the acetic acid derivative.

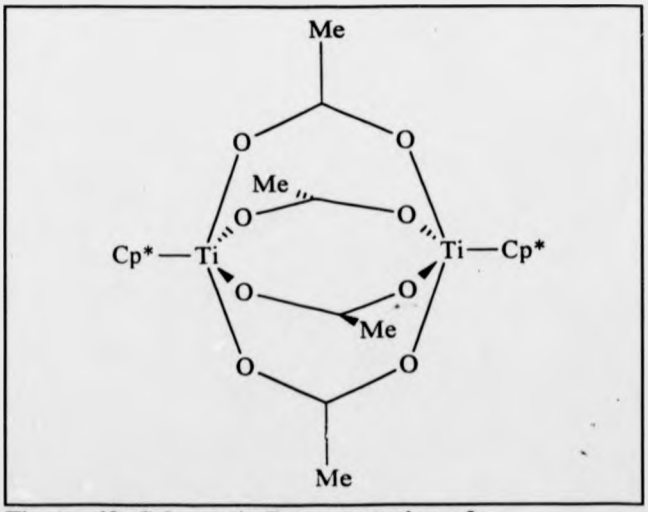


Figure 49. Schematic Representation of $[\{Cp^*Ti(O_2CMe)_2\}_2]$

In summary, the work of Wallbridge *et al* provides a wide range of carboxylate species including dinuclear compounds,[216] oxo titanium compounds[217-219] and various halo carboxylate species for example $[TiCl_3(O_2CR)]_3$ R = Ph, Me_3C, *o*-MeC_6H_4, *p*-MeC_6H_4 and *p*-ClC_6H_4.[220]

Wallbridge *et al*[218] reported a somewhat unexpected route to a range of titanium oxo cluster compounds, demonstrating the existence of a new Ti_4O_2 core through the isolation of $[Ti_4Cl_6(\mu_2\text{-}O_2CPh)_6(\mu_3\text{-}O)_2]$. Diversifying the range of acids suggests that the formation of oxo cluster compounds is dependant on the substituent supported by the aryl ring. Under similar conditions, the acid 2-$MeC_6H_4CO_2H$ yields $[Ti_4Cl_5(O_2CC_6H_4Me\text{-}2)_7O_2]$ while 4-$Bu^tC_6H_4CO_2H$ gives $[Ti_2Cl_2(O_2CC_6H_4Bu^t\text{-}4)_4O]$.[218] Prior to this, most known Ti oxo clusters incorporated a Cp or Cp^* moiety as in $[Cp^*TiBr(\mu\text{-}O)]_4{\cdot}CHCl_3$ which contains a Ti_4O_4 ring.[164]

Halo carboxylate species are prepared by the reaction of $TiCl_4$ with the desired acid. Careful control of the reaction conditions permits the isolation of a series of mono, bis and trischloro carboxylated species using stoichiometries of 1:1, 1:2 and 1:3 respectively. Subsequent hydrolysis affords many interesting compounds. Controlled hydrolysis of either $TiCl_3(O_2CMe)$ or $TiCl_2(O_2CMe)_2$ leads to the dinuclear compound $[Ti_2(\mu\text{-}O)(\mu\text{-}O_2CMe)_2Cl_4]{\cdot}2L$.[216] The μ-oxo compound of $TiCl_3(O_2CMe)$ arises from hydrolysis of the Ti-Cl bond whilst it is the Ti-carboxylate bond which is cleaved in the bischlorocarboxylate compound.

Other cluster compounds have been formed without bulky stabilising groups or hydrolysis. The tetranuclear oxo cluster $[Ti_4Cl_6(\mu\text{-}O_2CPh)_6(\mu_3\text{-}O)_2]$ is isolated from the reaction between $TiCl_4$ and benzoic acid (1:2 molar ratio) at moderate temperature (100-150°C).[218]

RESULTS AND DISCUSSION

Reaction of Cp^*TiMe_3 with *p*-Toluic Acid (where $Cp^* = 1,3\text{-}(t\text{-}Bu)_2Cp$)

The particular reaction system studied in Alcalá involved preparation of Cp^*TiMe_3 from Cp^*TiCl_3 and LiMe and subsequent reaction with *p*-toluic acid (1:3). Addition of the acid caused an evolution of gas (CH_4) with immediate colour change from yellow to deep red and finally to brown. The precipitate which appeared, after concentrating the solution *in vacuo*, was recrystallised from toluene/hexane affording colourless crystals.

IR Data

Four bands are observed in the carboxylate stretching region at 1609, 1582, 1517 and 1490 cm^{-1}, the latter of which is assigned to $\nu_{asym}(CO_2^-)$ stretching. The accompanying $\nu_{sym}(CO_2^-)$ stretching band cannot be unequivocally assigned as it is masked by the Nujol bands but it cannot exceed 1380 cm^{-1}. Commonly, the magnitude of the separation (Δ) of the symmetric and asymmetric $\nu(CO_2^-)$ stretching bands relative to that of the ionic value is used to determine the bonding mode. It has been proposed that Δ values greater than the ionic value are indicative of unidentate coordination whilst values which are lower signify chelating or bridging carboxylate groups. The above conclusions were drawn by Deacon and Philips[221] following their comprehensive review of the literature in which they attempted to correlate carboxylate stretching frequencies with their bonding modes. They found that acetate complexes with Δ values greater than 200 cm^{-1} invariably had unidentate coordination of some or all the acetate groups, whilst bidentate groups were found in compounds with Δ values lower than the ionic value. In our case the maximum Δ value equates to 110 cm^{-1}.

Many studies concerning coordination of acetate groups correlate Δ values of this magnitude (110 cm^{-1}) with a bidentate chelating mode. (Table 30)

Table 30. Selected Carboxylate Compounds and their Corresponding IR Δ Values

Compound	Δ Value	Ref
$Cu(O_2CMe)(Ph_3Ph)_2$	131	222
$Ni(O_2CMe)(tet)ClO_4$	102	223
$Sn(O_2CMe)_4$	120	224
$Zn(O_2CMe)_2(H_2O)_2$	94	225

tet=5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane

By analogy, a bidentate chelating mode is tentatively assigned to the *p*-toluic acid in this instance.

^{1}H NMR Data

The ^{1}H NMR spectrum obtained in deuterated benzene contained five types of resonances. As the Cp^* resonance was quite broad, the signal was not integrated. Comparison of the integral values for CH_3 and *t*-Bu substituents (0.13:0.68 = 1:5.2) with the theoretical values of 1:6 suggest an equal ratio of carboxylic acid to Cp^*. As shown in Table 31 the microanalytical data does not correspond well with that expected for the desired product $[Cp^*Ti(O_2CPhMe)_3]$. However it does correlate very well with a compound of empirical formula $C_{42}H_{56}O_6Ti_2$ relating to a hydrolysis product with the formulation $[Cp^*Ti(C_8H_7O_2)(\mu\text{-}O)]_2$.

Table 31. Microanalytical Data for $[Cp^*Ti(O_2CPhMe)(\mu\text{-}O)]_2$

Compound	Analytical Data (%) C	H
$[Cp^*Ti(O_2CPhMe)_3]$ (calc)	70.47	6.71
$[Cp^*Ti(O_2CPhMe)(\mu\text{-}O)]_2$ (calc)	67.02	7.50
$[Cp^*Ti(O_2CPhMe)(\mu\text{-}O)]_2$ (obs)	67.37	7.46

X-Ray Crystallography

Figure 51 displays a view of the compound with selected bond distances and angles placed in Table 33. The structure shows a dinuclear complex in which the titanium atom is seven coordinate. This arises from the coordination of a bidentate carboxylate group, a Cp^* moiety considered as a tridentate ligand and two oxygen bridges. The $Ti\text{-}O_{carboxylate}$ bond distances range from 2.116 to 2.133Å (mean 2.125 Å) and bear a close resemblance to those in $[Cp^*Ti(O_2CPh)_3]$ *cf.* 2.095(6) to 2.206(6) (mean 2.152 Å).[211] The Cp^* group is symmetrically bonded to the metal, with a titanium-ring centroid distance of 2.03 Å. The internal distances and angles within the Cp^* and carboxylate ligands deserve no special comments, except to say the C-O distances are almost equivalent 1.276(7) Å (O_1-C_{11}) and 1.270(7) Å (O_2-C_{11}).

The dimensions of this Ti_2O_2 unit correspond closely with those for the complex $[\{TiCl(\mu\text{-}O)(12\text{-}C\text{-}4)\}_2][SbCl_6]_2$, (Chapter 3) in which the titanium atoms are also seven coordinate. The Ti_2O_2 core is represented in Figure 50 and the dimensions of both compounds are listed in Table 32 to illustrate the similarity.

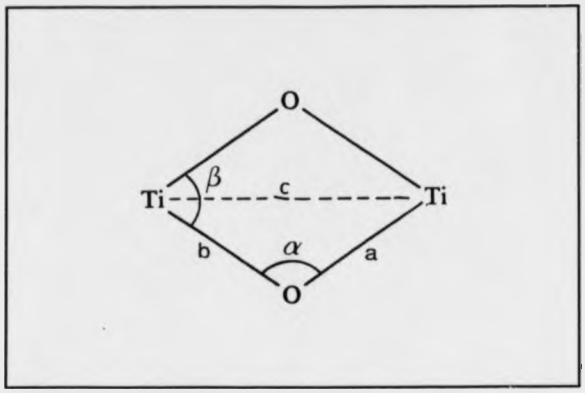


Figure 50. Dimensions of the Ti_2O_2 Core Unit

Table 32. Dimensions in Ti_2O_2 Core Units

Bonding Dimensions	Complex	
	$[\{TiCl(\mu\text{-}O)(12\text{-}C\text{-}4)\}_2][SbCl_6\}_2$	$[Cp^*Ti(C_8H_7O_2)(\mu\text{-}O)]_2$
a (Å)	1.823(4)	1.822(4)
b (Å)	1.811(3)	1.845(3)
c (Å)	2.789(2)	2.742(2)
α (°)	100.3(2)	96.8(2)
β (°)	79.7(2)	83.2(2)

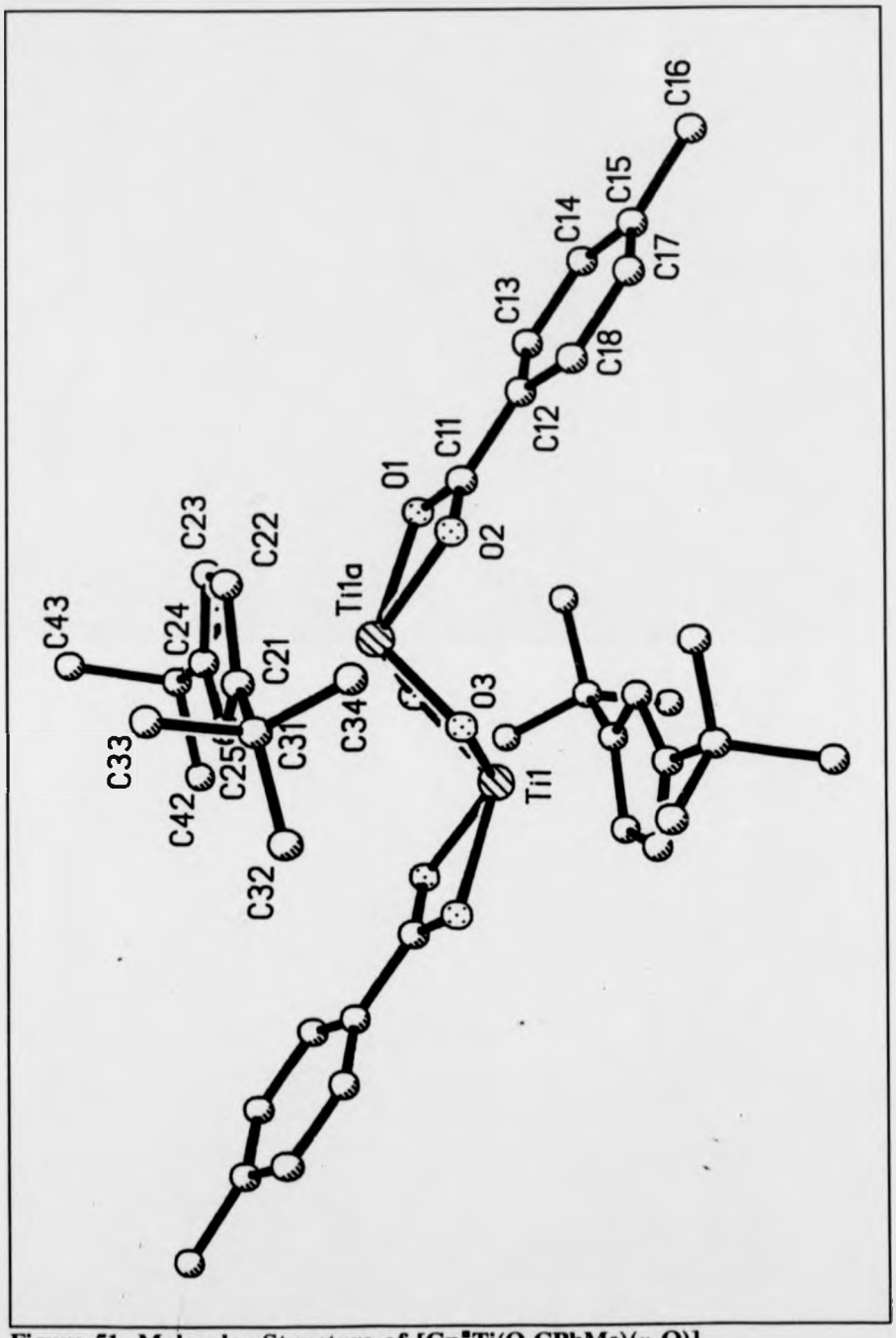


Figure 51. Molecular Structure of $[Cp^{*}Ti(O_2CPhMe)(\mu\text{-}O)]_2$

Table 33. Selected Bond Lengths (Å) and Angles (°) for

[Cp"Ti(O_2CPhMe)(μ-O)]$_2$

Ti(1)-O(3)#1	1.822(4)
Ti(1)-O(3)	1.845(4)
Ti(1)-O(1)#1	2.116(4)
Ti(1)-O(2)#1	2.133(4)
Ti(1)-C(25)#1	2.341(6)
Ti(1)-C(22)#1	2.368(6)
Ti(1)-C(21)#1	2.370(6)
Ti(1)-C(23)#1	2.378(6)
Ti(1)-C(24)#1	2.397(6)
Ti(1)-C(11)#1	2.491(6)
Ti(1)-Ti(1)#1	2.742(3)
O(1)-C(11)	1.276(7)
O(3)#1-Ti(1)-O(3)	83.2(2)
O(3)#1-Ti(1)-O(1)#1	127.0(2)
O(3)-Ti(1)-O(1)#1	87.9(2)
O(3)#1-Ti(1)-O(2)#1	87.5(2)
O(3)-Ti(1)-O(2)#1	131.9(2)
O(1)#1-Ti(1)-O(2)#1	61.3(2)
Ti(1)#1-O(3)-Ti(1)	96.8(2)
C(23)-C(24)-Ti(1)#1	72.3(4)
C(25)-C(24)-Ti(1)#1	70.5(4)
C(41)-C(24)-Ti(1)#1	125.8(4)
C(21)-C(25)-C(24)	110.8(6)
C(21)-C(25)-Ti(1)#1	74.0(4)
C(24)-C(25)-Ti(1)#1	74.9(4)
C(21)-C(31)-C(32)	111.0(6)
C(21)-C(31)-C(34)	112.1(5)
C(32)-C(31)-C(34)	108.5(6)
C(21)-C(31)-C(33)	107.3(5)
C(32)-C(31)-C(33)	109.3(6)
C(34)-C(31)-C(33)	108.6(6)
C(42)-C(41)-C(24)	112.4(6)
C(42)-C(41)-C(44)	109.2(6)
C(24)-C(41)-C(44)	111.2(6)
C(42)-C(41)-C(43)	109.1(6)
C(24)-C(41)-C(43)	105.7(6)
C(44)-C(41)-C(43)	109.1(6)

CHAPTER EIGHT

EXPERIMENTAL

EXPERIMENTAL

General Procedures

Unless otherwise stated all compounds are air/moisture sensitive. All manipulations with these compounds were carried out using an all glass Schlenk system and/or a conventional dry box flushed with dry nitrogen (2-4 ppm H_2O) and whose atmosphere was monitored by P_2O_5.

Solvents

All solvents were obtained from FSA, Loughborough with the exception of MeCN and THF which were supplied by Rathburn Chemical Co Ltd, Walkerburn, Scotland and May and Baker, Manchester, respectively. Each solvent was stored over and distilled from a suitable drying agent under an atmosphere of nitrogen prior to use, as detailed below, (Table 34)

Table 34. Solvent Drying Agents

Solvent	Drying Agent
MeCN, Dichloromethane, *n*-hexane, *n*-pentane	Calcium Hydride
Benzene, Toluene	Sodium Wire
Diethyl-ether, THF	Na/K alloy with benzophenone

Reagents

All reagents were obtained from Aldrich Chemical Company, Gillingham and used as supplied unless otherwise stated.

Instrumentation

Melting points were recorded on an Electrothermal melting point apparatus.

Infrared spectra were recorded as either Nujol or halocarbon mulls located between CsI plates on a Perkin-Elmer 580B instrument from 4000-200 cm^{-1}.

Proton (^1H) NMR were recorded using a Bruker 240 MHz spectrometer with deuterated solvent signals used as the reference standards.

UV Visible spectroscopic measurements were made with a Phillips PU 8720 UV/VIS scanning spectrophotometer using MeCN solutions, sealed in quartz cells of 1 cm path length.

Analytical Techniques

Elemental analysis (C, H, N, Cl %) was carried out by Medac Ltd, Brunel University. Small samples were sealed in glass tubes under argon to prevent deterioration of the compound in transit. The titanium content of samples was determined by utilizing the absorbance of titanium(IV) peroxo-species $[TiO(SO_4)_2]^{2-}$ at 410 nm in acid solutions, between concentrations of 10-100 ppm Ti; these yellow solutions obey the Beer-Lambert law. A small portion of the accurately weighed test sample (0.01-0.1g) was hydrolysed with concentrated sulphuric acid (8 cm^3), a drop of H_2O_2 (20 vol) was added and the solution made up to 100 cm^3 with distilled water. The absorbance of the resulting yellow

solution in a 1 cm^3 polycarbonate cuvette was measured with a Pye-Unicam SP6-250 spectrophotometer and compared with standards.

Spot tests for antimony were carried out by addition of zinc powder to a dilute sulphuric acid solution of the test compound to cause regular evolution of hydrogen. A plug of cotton wool moistened with aqueous $AgNO_3$ was placed over the top of the test tube. A black spot of metallic Ag confirms the presence of Sb due to the production of SbH_3.

EXPERIMENTAL CHAPTER TWO

Preparation of $TiCl_4(MeCN)_2$

This adduct was prepared following a method adapted from the preparation of $TiCl_4(THF)_2$ by Manzer.[226] A solution of $TiCl_4$ (5.02g, 26.46 mmol) in dichloromethane (50 cm^3) was added to a Schlenk vessel equipped with a magnetic stirrer bar. Freshly distilled MeCN (25 cm^3) was added dropwise and the solution stirred at room temperature under nitrogen for 30 minutes. Dry hexane (75 cm^3) was added and the solution chilled to (-25°C) for 1 hour. A bright yellow solid deposited. This was collected by filtration and washed with hexane (2 x 25 cm^3). The solid was dried *in vacuo*. A second crop of product was isolated from the mother liquors following concentration *in vacuo* and addition of hexane (50 cm^3). The total yield was 6.65g, 92.49%. Colour, yellow, M.p. 145-147°C, ν_{max}(CN) 2310m, 2303m, 22830m, 2275m, ν_{max}(MCl) 405sh, 390s,(br), 320w cm^{-1} (Nujol).

The MeCN adducts of $ZrCl_4$, $HfCl_4$ and $SnCl_4$ were prepared in a similar manner to $TiCl_4(MeCN)_2$. The spectroscopic and analytical details for the *bis* adducts are given in Table 35. In some instances the tetrachlorides were used as supplied.

Table 35. Metal Tetrachloride Adducts of MeCN (M=Ti, Zr, Hf and Sn)

Adduct	Yield g, (%)	IR (cm^{-1})	Analytical Data calc/obs (%)		
			C	H	N
$TiCl_4(MeCN)_2$	6.65, 92.48	2310m, 2303m, 2283m, 2275m, 1025w, 938w, 405sh, 390s, br, 320w	17.68, 17.54	2.22, 2.13	10.31, 10.22
$ZrCl_4(MeCN)_2$	11.71, 85.78	2310m, 2282m, 1024m, 946m, 414w, 350s,br, 315sh	15.25, 15.01	1.92, 1.74	8.89, 8.64
$HfCl_4(MeCN)_2$	11.66, 88.40	2311s, 2282s, 1025m, 945m, 414w, 350s,br, 315sh	11.94, 11.83	1.50, 1.47	6.96, 6.86
$SnCl_4(MeCN)_2$	8.24, 90.71	2312s, 2280m, 1024m, 937m, 410m, 345s, 334vs, 303m	14.02, 13.89	1.77, 1.64	8.18, 8.01

Preparation of $[TiCl_3(MeCN)_3][SbCl_6]$

A solution of $SbCl_5$ (4.74g, 15.85 mmol) in MeCN (25 cm^3) was added dropwise to a chilled (-30°C) stirred solution of $TiCl_4(MeCN)_2$ (4.31g, 15.86 mmol) in MeCN (25 cm^3). The yellow solution was stirred for 3 hours under nitrogen. Complete solvent removal *in vacuo* gave an oily yellow mass which was washed with hexane (3 x 50 cm^3) and dried *in vacuo*. The product was recrystallised from MeCN and CH_2Cl_2 yielding yellow needle crystals.

Yield 4.49g, 46.29%, Mpt 96-97°C. Found: C, 12.04; H, 1.59; N, 6.03; Cl, 52.47. Calc for $C_6H_9N_3Cl_9SbTi$: C, 11.78; H, 1.48; N, 6.87; Cl, 52.15%. ν_{max}(CN) 2322s, 2299s, ν_{max}(M-Cl) 431m, 345s, (br) cm^{-1} (Nujol). λ_{max} 269.7 nm, 37,078cm^{-1} (MeCN).

The reactions of $ZrCl_4$, $HfCl_4$ and $SnCl_4$ with one equivalent of $SbCl_6$ were carried out in a similar manner to the reaction with $TiCl_4$. The reaction details are given in Table 36, and the spectroscopic results are listed in Table 37.

Table 36.

Synthetic Details for Reaction of MCl_4 (M = Zr, Hf and Sn) with $SbCl_5$

Mass of $MCl_4(MeCN)_2$ g, mmol	Mass of $SbCl_5$ g, mmol	Colour	Yield of Initial Product g, %
$TiCl_4$ 4.31g 15.86mmol	4.74g 15.85mmol	Yellow	4.49, 46.24
$ZrCl_4$ 0.62g 1.97mmol	0.59g 1.97mmol	Off White	0.62, 48.06
$HfCl_4$ 0.61g 1.52mmol	0.45g 1.50mmol	Off White	0.84, 74.60
$SnCl_4$ 0.65g 1.90mmol	0.57g 1.91mmol	Buff	0.63, 48.46

Yields are based on products with the formulation $[MCl_3(MeCN)_3][SbCl_6]$.

Table 37. Analytical and Spectroscopic Data for $[MCl_3L_x][SbCl_6]$, x=3 for Ti and Sn, x=4 for Zr and Hf

Product	UV-Vis nm/cm^{-1}	Analytical Data calc/obs (%) C H N Cl	IR (cm^{-1})
$[TiCl_3L_3][SbCl_6]$ L=MeCN	269.7 37,078	11.78, 1.48, 6.87, 52.15 12.04, 1.59, 6.03, 52.47	2322m, 2299m, 1062m, 972w, 829m, 430m, 428m, 345s, br, 310sh
$[ZrCl_3L'_4][SbCl_6]$ L=1,4-dioxane	270.5 36,969	21.73, 3.65, /, 36.08 21.96, 4.00, /, 36.19	1295m, 1258m, 1108s, 1075s, 1045m, 892m, 815w, 724w, 620m, 535w, br, 470w, 345s, 280m
$[HfCl_3L'_5][SbCl_6]$ L=1,4-dioxane	270.7 36,982	22.67, 3.80, /, 30.11 22.80, 4.37, /, 30.97	1295m, 1110s, 1077m, 1043w, 890w, 811w, 622m, 422m, 345s, br, 300w,sh
$[SnCl_3L_3[SbCl_6]$ L=MeCN	269.9 37,051	10.56, 1.33, 6.16, 46.74 10.43, 1.29, 6.09, 46.65	2322m, 2295m, 1295s, 1258s, 1105s, 1075s, 1042m, 895m, 855s, br, 823w, 624m, 485w, 440w, 425w, 345s, br, 312s,

Several other halide abstracting agents were used in an attempt to isolate monocation salts with non-redox anions. The reaction of $TiCl_4$ with $NaBPh_4$ is described in detail and provides a general illustration of the procedures used.

Reaction of $TiCl_4$ with $AgBPh_4$

A solution of $AgBPh_4$ (0.9g, 2.10 mmol) in MeCN (10 cm^3) was added dropwise via a transfer needle to a stirred solution of $TiCl_4$ (0.4g, 2.11 mmol) in MeCN (30 cm^3) at room temperature under a nitrogen atmosphere. This resulted in the immediate precipitation of AgCl (0.28g, 92.72%). The reaction was concentrated *in vacuo*, cooled in an ice bath and filtered through Celite. The liquors were layered with an equal volume of hexane. After standing for 24 hours at -25°C a pale yellow powder precipitated. The liquors were removed and the solid washed with hexane (2 x 25 cm^3). The pale yellow solid was dried *in vacuo*. Yield 0.84g, 66.67%.

The synthetic details for reactions of $TiCl_4$ with $AgBF_4$, $AgCF_3SO_3$ and $NaBPh_4$ are listed in Table 38. The analytical and spectroscopic results are listed in Tables 39 and 40 respectively. The reactions were not attempted with $ZrCl_4$, $HfCl_4$ or $SnCl_4$.

Table 38. Synthetic Details for Reaction of $TiCl_4$ with Halide Abstracting Agents

$TiCl_4$ g, mmol	Halide Abstracting Agent g, mmol	Yield AgCl g, %	Product Yield After Recrystallisation g, %
0.40, 2.11	$AgBPh_4$ 0.9, 2.11	0.28 92.72	0.84, 66.67
0.41, 2.16	$AgBF_4$ 0.42, 2.16	0.25, 80.65	0.42, 42.42
0.51, 2.69	$AgCF_3SO_3$ 0.69, 2.69	0.32, 82.05	0.44, 42.47
0.28, 1.48	$NaBPh_4$ 0.50, 1.46	0.11, 52.38	0.28, 31.78

Table 39. Analytical Data for Titanium Monocations.

Compound	Analytical Data C H N Cl Ti calc/obs (%)
$(TiCl_3L_3)(BPh_4)$ (I)	60.39, 4.90, 7.04, 17.83, 8.03 59.89, 4.65, 6.25, /, 7.87
$(TiCl_3L"_3)(BF_4)$ (II)	31.51, 5.29, /, 23.58, 10.47 29.98, 5.07, /, /, /
$(TiCL_3L_2)(CF_3SO_3)$ (III)	15.58, 1.57, 7.27, 27.60, 12.42 15.05, 1.78, 6.34, /, /
$(TiCl_3L_3)(BPh_4)$ (IV)	60.39, 4.90, 7.04, 17.83, 8.03 59.68, 4.66, 6.23, /, 7.81

L = MeCN, L" = THF

Table 40. Infrared Data for Titanium Monocations

Compound	IR cm^{-1}
(I)	2362m, 2316m, 1967w, 1918w, 1710w, 1698w, 698s, 355sh, 345s, br
(II)	1175m, 1017s, 921m, 834m, 505s, 370sh, 345s, br
(III)	2320s, 2290s, 1350s, 1236s, 1236s, 1192s, 1136s, 1010s, 947m, 765m, 400s, br, 345sh, 320w, 280w
(IV)	2361m, 2315m, 1967w, 1918w, 1710w, 1699w, 699s, 669s, 355sh, 345s, br

Preparation of $TiCl_3(MeCN)_3$

The adduct $TiCl_3(MeCN)_3$ was obtained by Soxhlet extraction of $TiCl_3$ (1.76g, 11.41 mmol) with MeCN (270 cm^3). The deep blue solution which formed yielded blue crystals of the adduct on cooling to 0°C. A second crop was obtained by concentrating the mother liquors to 100 cm^3 and cooling to 0°C. A total yield of 2.64g, 83.28% was obtained. Mpt = 138-139°C, ν_{max}(CN) 2313s, 2283s, cm^{-1} (Nujol), λ_{max}(MeCN) 608nm, 582nm, (14,700, 17,195 cm^{-1}), Found Ti, 17.18% calc for $C_6H_9N_9Cl_3Ti$ 17.27%.

Reaction of $TiCl_3(MeCN)_3$ with $SbCl_5$

Dissolution of $TiCl_3(MeCN)_3$ (1.5g, 5.41 mmol) in MeCN (25 cm^3) gave a bright blue solution to which was added $SbCl_5$ (0.81g, 2.71 mmol) in MeCN (15 cm^3). This resulted in an immediate colour change to green then yellow after 5 minutes. The solution was stirred at room temperature for 6 hours. Solvent removal *in vacuo*

gave a sticky yellow solid which was washed with toluene (3 x 25 cm^3) followed by hexane (3 x 25 cm^3). Pumping the solid under vacuum for 3 hours yielded a finely divided yellow solid. ν_{max}(CN) 2311m, 2304m, 2283m, 2275m, ν_{max}(M-Cl) 405sh, 390s, (br), 320w cm^{-1} (Nujol).

Reaction of $TiCl_3(MeCN)_3$ with $NaBPh_4$

A solution of $NaBPh_4$ (0.6g, 1.75 mmol) in MeCN (25 cm^3) was slowly added to a stirred solution of $TiCl_3(MeCN)_3$ (0.49g, 1.77 mmol) in MeCN (25 cm^3). The mixture was allowed to stir at room temperature for 24hours. The reaction mixture was concentrated by solvent removal and placed in a freezer at -25°C, which resulted in the precipitation of a bright blue solid. This was collected by filtration and washed with hexane (3 x 25 cm^3) and dried *in vacuo*. The examination of the blue product by UV and IR spectroscopy showed little difference when compared with the spectra of $TiCl_3(MeCN)_3$. Mpt 138-139°C, ν_{max}(CN) 2325, 2290, cm^{-1} (Nujol), λ_{max} 608nm, 582nm (14,703 and 17,194 cm^{-1}) (Lit 14,700 and 17,200 cm^{-1}).

REMOVAL OF THREE CHLORIDE IONS

Reaction of $TiCl_4$ with excess $SbCl_5$

(Method 1)

A solution of $TiCl_4$ (1.99g, 10.49 mmol) in MeCN (30 cm^3) was added to a stirred solution of $SbCl_5$ (15.68g, 52.4 mmol) in MeCN (20 cm^3). The mixture was stirred for 24 hours resulting in a pale brown solution. A tacky green/brown solid was obtained after removing the solvent under vacuum. When washed with toluene (3 x 20 cm^3) followed by hexane (3 x 20 cm^3) and dried *in vacuo* khaki powder

remained. Dissolution in MeCN (25 cm^3) and layering with an equal volume of CH_2Cl_2 affords emerald green cubic crystals.

Yield 7.22g, 53.28%. Mpt 85-86°C. ν_{max}(CN) 2322m, 2298m, ν(M-Cl) 423m, 345s, (br) cm^{-1} (Nujol). λ_{max} 269.8nm, 37,064 cm^{-1}.

(Method 2)

The reagent $SbCl_5$ (4.60g, 15.39 mmol) was added to a stirred solution of $[TiCl_3(MeCN)_3][SbCl_6]$ (9.41g, 15.39 mmol) in MeCN (15 cm^3). Solvent removal after 24 hours gave a yellow oily mass. Washing with toluene (3 x 20 cm^3) and drying *in vacuo* gave a lime coloured powder. Recrystallisation from $MeCN/CH_2Cl_2$ yields the same crystals as obtained using method 1. Yield 6.22g, 31.30%.

In both cases the crystals are extremely difficult to handle without deterioration, forming a powder when removed from the mother liquors or washed with fresh solvent.

Preparation of the tricationic species of $ZrCl_4$, $HfCl_4$ and $SnCl_4$ was attempted following the above procedure. The experimental details are listed in Table 41. The products were extremely difficult to handle and therefore not pursued further.

Table 41. Synthetic Details for Tricationic Reactions

Reaction 1:5	Mass of MCl_4 g, mmol	Mass of $SbCl_5$ g, mmol	Yield g, %
$TiCl_4$: $SbCl_5$	1.99, 10.49	15.68, 52.45	7.22 53.28
$ZrCl_4$: $SbCl_5$	1.56, 6.69	10.01 33.48	2.08 23.27
$HfCl_4$: $SbCl_5$	1.52, 4.75	7.10 23.74	1.75 25.93
$SnCl_4$: $SbCl_5$	2.54, 9.75	14.58 48.76	4.86 36.57

Table 42. Analytical and Spectroscopic Data for $[TiClL_5][SbCl_6]\cdot 2L$

Product	UV-Vis nm cm^{-1}	Analytical Data calc/obs (%) C H N	IR cm^{-1}
$[TiClL_5][SbCl_6]_3\cdot 2L$	269.8, 37,147	12.24, 1.54, 7.14 12.56, 1.66, 7.31	2322m, 2298m, 1266m, 1040w, 947w, 740s, 428s, 423s, 345s,br, 340s

EXPERIMENTAL FOR CHAPTER THREE

Preparation of Crown Ether Complexes of $[TiCl_3(MeCN)_3][SbCl_6]$

The complexes were prepared by direct addition of an acetonitrile solution of the appropriate crown ether to a stirred solution of the titanium cation in acetonitrile. To illustrate the general procedure, the reaction of 12-crown-4 with the titanium cation is described here.

Reaction of $[TiCl_3(MeCN)_3][SbCl_6]$ with 12-crown-4.

The 12-crown-4 (0.37 g, 2.10 mmol) in MeCN (25 cm^3) was added dropwise to a cold (solid CO_2-acetone) solution of $[TiCl_3(MeCN)_3][SbCl_6]$ (1.30 g, 2.12 mmol) in MeCN (30 cm^3). The resulting solution was allowed to warm to room temperature and stirred for 24 hours. Removal of solvent gave a pale yellow solid which was washed with pentane (3 x 25 cm^3) and pumped dry *in vacuo*. The crude product was dissolved in the minimum volume of MeCN (*ca* 20 cm^3) and layered with an equal volume of CH_2Cl_2. Large colourless block crystal formed within 3 hours and were collected by filtration and pumped dry *in vacuo*. Yield, 0.56 g, 37.9%

(Found: C, 15.65; H, 2.80; Cl, 45.80; Ti, 6.60. Calc. for $[\{TiCl(\mu\text{-}O)(12\text{-crown-}4)\}_2][SbCl_6]_2 = C_{18}H_{36}Cl_{18}O_{10}Sb_2Ti_2$: C, 15.55; H, 2.60; Cl, 45.90; Ti, 6.90%). ν_{max} 1259m, 1255w, 1250w, 1128m, 1065s, 1030m, 950m, 920w, 875m, 825w, 785m, and 345vs (br) cm^{-1} (Nujol). $\delta(CD_3CN)$ 3.70 (16H,s, CH_2 of crown). λ_{max}(MeCN) 262.5nm, (38,100 cm^{-1}).

The reactions with 15-crown-5 and 18-crown-6 were performed in an identical manner to that described for 12-crown-4, and the details are summarised in Table 43. Analytical and spectroscopic data for the resulting complexes are listed in Tables 44 and 45 respectively.

Table 43. Experimental Details for Crown Ether Reactions with $[TiCl_3(MeCN)_3][SbCl_6]$

$[TiCl_3(MeCN)_3][SbCl_6]$ g, mmol	Crown g, mmol	Product (Yield g, %)
1.30, 2.12	12-C-4 0.37, 2.10	$[\{TiCl(\mu\text{-}O)(12\text{-}C\text{-}4)\}_2][SbCl_6]_2$ (I) (0.56, 37.9)
0.83, 1.36	15-C-5 0.30, 1.36	$[\{TiCl(\mu\text{-}O)(15\text{-}C\text{-}5)\}_2][SbCl_6]_2$ (II) (0.36, 40.45)
1.30, 2.12	18-C-6 0.56, 2.12	$[H_3O^+(18\text{-}C\text{-}6)][SbCl_6]$ (III) (1.1, 83.97)

Table 44. Analytical Data for Crown Ether Reactions with $[TiCl_3(MeCN)_3][SbCl_6]$

Complex	C (%)	H (%)	Cl (%)	Ti (%)
$[\{TiCl(\mu\text{-}O)(12\text{-}C\text{-}4)\}_2][SbCl_6]_2 \cdot 2L$ (I)				
Calculated	15.56	2.61	45.91	6.89
Observed	15.65	2.80	45.80	6.60
$[\{TiCl(\mu\text{-}O)(15\text{-}C\text{-}5)\}_2][SbCl_6]_2$ (II)				
Calculated	18.36	3.08	/	7.32
Observed	18.67	3.37	/	6.76
$[H_3O^+(18\text{-}C\text{-}6)][SbCl_6]$ (III)				
Calculated	23.34	4.41	34.43	/
Observed	23.82	4.50	34.40	/

L = CH_2Cl_2

Table 45. Spectroscopic Data for Crown Ether Reactions with $[TiCl_3(MeCN)_3][SbCl_6]$

Compound	Colour	UV-VIS nm cm^{-1}	^1H NMR (δ) (CD_3CN)	IR (cm^{-1})
12-C-4	colourless liquid	/	3.57	2904vs, 2863vs, 1469vs, 1450s, 1363m, 1289m, 1250m, 1136vs, 1094vs, 1023s, 913vs, 844s, 546m
15-C-5	colourless liquid	/	3.55	2862m, 1450s, 1356s, 1300m,br, 1280w, 1251s, 1119vs, 1087s, 1037w, 980m, 941s, 854s, 517m,
18-C-6	white needle crystals	/	3.51	1354m, 1346m, 1298m, 1279w, 1261m, 1239m, 1222w, 1142sh, 1127sh 1110vs, 1078sh, 1060w, 1042w, 992s, 902m, 889w, 863s, 832m, 570m, 538m, 465m
(I)	colourless crystal	262.5 38,100	3.70	1259m, 1255w, 1250w, 1128m, 1065s, 1030m, 950m, 920w, 907m, 875m, 815w, 785m, 345vs,br
(II)	buff powder	insol	insol	1275w, 1248w, 1135w, 1128s, 1120w, 1105m, 1090m, 1065s, 1033m, 982s, 936m, 908m, 832m, 709s, 433m, 345vs,br
(III)	colourless crystals	270.1 37,022	3.53 10.1	1288w, 1200w, 1140m, 1095m, 1080sh, 970m, 945w, 839w, 345s,br

EXPERIMENTAL FOR CHAPTER FOUR

The crown thioether ligands 9-S-3 and 18-S-6 were prepared as outlined below. The ligands 12-S-4 and 15-S-5 were obtained from the Aldrich Chemical Company.

Preparation of 1,4,7-Trithiacyclononane (9-S-3) and 1,4,7,10,13-Hexathiacylododecane (18-S-6)

The ligands were prepared following the method of Cooper *et al.*[227]

The reagent 1,4,7-trithiaheptane (5.56g, 36 mmol) and 1,2-dichloroethane (3.54g, 36 mmol) were dissolved in DMF (250 cm^3). The resulting solution was added at constant rate over 72 hours, under nitrogen to a vigorously stirred suspension of caesium carbonate (13.03g, 40 mmol) in the same solvent (150 cm^3) at 70°C. After complete addition, the solvent was removed by vacuum distillation, followed by pumping on a high vacuum line for several hours. The residue was slurried with dichloromethane (300 cm^3) and the insoluble caesium salts removed by filtering through Celite. The resulting solution was washed successively with dilute sodium hydroxide solution and water, dried with anhydrous sodium sulphate and evaporated. 9-S-3 was sublimed from the residue at 90°C under vacuum, condensing on a water cooled cold finger as fibrous crystals, 2.24g, 34% (^{1}H NMR 250 MHz, $\delta(CDCl_3)$, 3.13, M.p. 80-81°C, Mass spec. $^m/_e$ 180).

The ligand 18-S-6 was isolated from the sublimation residue by column chromatography (CH_2Cl_2/SiO_2). Evaporation of the 18-S-6 fractions yielded 0.65g (10%) of colourless needles. (^{1}H NMR 250 MHz, $\delta(CDCl_3)$, 2.82, M.p. 90-91°C, Mass spec. $^m/_e$ 360).

In the above procedure dichloromethane can be replaced with 1,2-dichloroethane obtaining similar yields but an elevated temperature (100°C) is required.

Table 46. Spectroscopic Details of Crown Thioethers

Ligand	Colour	Mpt (°C)	^{1}H NMR δ (CD_3CN)	IR (cm^{-1})
9-S-3	white crystals	78-81	3.19 ($CDCl_3$)	923m, 875s, 824s
12-S-4	colourless liquid	226-228	2.72	1266m, 1204m, 1184m, 1182m, 1127m
15-S-5	white colourless crystals	122-127	2.76	1225w, 1192s, 1123m, 1020w, 945w, 887w, 692s, br,
18-S-6	white powder	92-94	2.81	1259w, 1265w, 1190w, 1145w, 925w, 840w, 680m

The metal tetrachlorides were reacted with the selected crown thioether following the same procedures. Of the reactions only three yielded a product other than unchanged ligand. The details of one such reaction ($TiCl_4$ with the ligand 9-S-3) was chosen to illustrate this procedure. The synthetic details for the other crown thioether reactions are listed in Table 47. The analytical and spectroscopic data are given in Table 48 and 49 respectively.

Reaction of $TiCl_4$ with 9-S-3

The solvent MeCN (30 cm^3) was placed in an adapted U-tube vessel under a nitrogen atmosphere. Titanium tetrachloride (0.264g, 1.39 mmol) in MeCN (10 cm^3) was added dropwise to one side-arm and 9-S-3 (0.25g, 1.39 mmol) in MeCN (10 cm^3) was similarly added to the other. On leaving the system undisturbed for several days, yellow dendritic crystals deposited at the bottom of the vessel. After removal of the mother liquors the product was carefully collected and washed with ether (10 cm^3) then hexane (2 x 10 cm^3) and dried *in vacuo*. Yield (0.222g, 43.11%). Anal: Calcd for $C_6H_{12}Cl_4S_3Ti$, C, 19.47, H, 3.27, Cl, 38.3. Found C, 19.45, H, 3.14, Cl 37.8%. ν_{max} 1409s, 1304w, 1290w, 1149w, 1020m, 938m, 905s, 780vs, 671w, 628m, 442s, 410vs, 396s, 365vs, (br) 330s, 280s cm^{-1} (Nujol).

Table 47. Synthetic Details for Reaction of Selected Crown Thioethers with MCl_4 (where M=Ti, Zr, Hf and Sn)

MCl_4 g, mmol	Thiocrown Ether g, mmol	Yield g, %
$TiCl_4$ 0.264, 1.390	9-S-3 0.250, 1.390	0.222, 43.11
$SnCl_4$ 0.155, 0.595	9-S-3 0.107, 0.594	0.097, 42.83
$SnCl_4$ 0.140, 0.538	18-S-6 0.192, 0.534	0.092, 39.0

Table 48. Analytical Data for the Crown Thioether Products

Compound	Analytical Data calc/obs (%) C, H, Cl, N
$TiCl_4$(9-S-3)	19.47, 3.27, 38.3, / 19.45, 3.14, 37.8, /
$[SnCl_3(9\text{-}S\text{-}3)]_2[SnCl_6]$	12.60, 2.10, 37.25, / 12.45, 2.10, 37.05, /
$2SnCl_4$·(18-S-6)	18.20, 2.95, 30.75, 1.50 18.10, 2.90, 30.30, 1.75

Table 49. IR Data for the Crown Thioether Products

Compound	IR (cm^{-1})
$TiCl_4$(9-S-3)	1409s, 1304w, 1290w, 1149w, 1020m, 938m, 905s, 780vs, 671w, 628m, 442s, 410vs, 396s, 365vs, br, 330s, 280s
$3(SnCl_4)2$(9-S-3)	1304w, 1289w, 1143w, 1081w, 971w, 929m, 891s, 821s, 661w, 436m, 345br, vs, 296vs, br,
$2(SnCl_4)$·(18-S-6)	1295w, 1262m, 1225m, 1205s, 1152m, 1130w, 1015w, 915m, 901m, 855s, 739s, 692w, 685s, 644w, 443m, 340sh, 330sh, 321vs, br, 272s, br, 251sh

Preparation of $[Fe(9\text{-}S\text{-}3)_2][Sb_2Cl_8]$

Method A

Acetonitrile (25 cm^3) was placed in an adapted U-tube vessel under a nitrogen atmosphere. A solution of $[TiCl_3(MeCN)_3][SbCl_6]$ (0.85g, 1.39 mmol) in MeCN (15 cm^3) was added dropwise to one arm and, concurrently, 9-S-3 (0.25g, 1.39 mmol) in MeCN (10 cm^3) was added to other. After several hours standing at room temperature the solution developed a deep red colour and a small crop of

maroon crystals (0.06g) deposited on the walls of the vessel. These were carefully collected, washed with ether (10 cm^3) and placed in a desiccator. A suitable crystal was selected for X-ray diffraction studies.

Method B

A solution of the ligand 9-S-3 (0.25g, 1.39 mmol) in MeCN (20 cm^3) was added dropwise to a solution containing $SbCl_5$ (0.42g, 1.40 mmol) and iron fillings (0.08g, 1.43 mmol) in MeCN (30 cm^3). The mixture was stirred with heating (60°C) for 24 hours to give a crimson/brown solution. Partial removal of solvent resulted in the deposition of the maroon product which was washed with ether (10 cm^3) and dried *in vacuo* . Recrystallisation from MeCN gave maroon-red platelet crystals which were amenable to X-ray diffraction studies. Yield 0.39g, 59.2%. Anal. Calcd. for $C_{12}H_{24}S_6FeSb_2Cl_8$. C,15.27, H, 2.56, Cl, 30.06. Found C, 15.18, H, 2.40, Cl, 29.92%. ν_{max} 922m, 875s, 340s cm^{-1} (Nujol).

EXPERIMENTAL FOR CHAPTER FIVE

Monoazacrown Ethers

Titanium tetrachloride was reacted with the selected monoazacrown ethers following the same procedures. The details of one such reaction ($TiCl_4$ with the ligand 1-aza-12-crown-4) was chosen to illustrate this procedure. Experimental details for all reactions are listed in Table 50 and the IR data for the free ligands and initial products is given in Table 23.

Reaction of $TiCl_4$ with 1-aza-12-crown-4

$TiCl_4$ (0.087g, 0.46 mmol) in MeCN (20 cm^3) was added dropwise to a solution of 1-aza-12-crown-4 (0.08g, 0.46 mmol) in the same solvent (30 cm^3) and the resulting solution stirred for 4 hours at room temperature. Removal of the solvent by slow evaporation yielded a powder which was washed with hexane (2 x 25cm^3) and dried *in vacuo*. Yield 0.1g, 66%. Found C, 28.83; H, 4.54; N, 4.05. $C_8H_{16}NO_3TiCl_3$ requires C, 29.25; H, 4.95; N, 4.26. ν_{max} 1284m, 1245m, 1150, 1128m, 1105, 1190m, 1095s, 1032m, 960w, 935m, 895m, 850w, 825m, 335s (br) cm^{-1} (Nujol). $\delta H(CD_3CN)$ 3.21 (4 H, CH_2^a), 3.58 (4 H, CH_2^b), 3.72 (4 H, CH_{2c}), 3.84 (4 H, CH_2^d).

Recrystallisation was attempted by dissolving the product in hot MeCN. The solution was filtered then allowed to stand at room temperature. On cooling a white powder deposited. The solid was collected and washed with hexane (2 x 25cm^3) then dried *in vacuo*. Yield 0.05g, 24%. ν_{max} ν(N-H) 3180m, ν(C-O-C) 1080m, ν(Ti-Cl) 340 cm^{-1} (Nujol). δH (CD_3CN) 8.96, (very broad. not integrated).

Table 50. Experimental Details For the Monoazacrown Ether Reactions with $TiCl_4$

$TiCl_4$ g, mmol	Monoazacrown Ether g, mmol	Initial Product Yield g, %
0.087, 0.46	0.08, 0.46	0.1, 66.7
0.13, 0.69	0.15, 0.68	0.18, 70.5
0.11, 0.58	0.15, 0.57	0.18, 74.4

Table 23. Infrared Data for Free Ligands and Initial Products

Compound	IR (cm^{-1})
1-aza-12-crown-4	3306m, 1288m, 1216m, 1113s, 1027s, 937m, 910m, 784m, 590m, 554m
1-aza-15-crown-5	3242m, 1293m, 1253m, 1216m, 1125s, 1041m, 941m, 847m, 778m, 564m, 517m
1-aza-18-crown-6	3332m, 1288m, 1250m, 1212m, 1110s, 955m, 888m, 842w, 778w, 519w
[$TiCl_3$(1aza-12-crown-4)]	1284m, 1245m, 1150m, 1095s, 1032m, 960m, 935m, 850m, 825m, 335s, br
[$TiCl_3$(1aza-15-crown-5)]	1290m, 1230m, 1110m, 1095s, 958m, 845m, 345br, s
[$TiCl_3$(1aza-18-crown-6)]	1378m, 1301m, 1288s, 1245s, 1088vs, 945s, 849m, 839s, 321vs, br

EXPERIMENTAL FOR CHAPTER SIX

Preparation of the complexes $[Mg(MeCN)_6][\{TiCl_4(MeCN)_2\}(\mu\text{-}O)]\cdot 4MeCN$ and $[TiCl_2(MeCN)_2(\mu\text{-}O)]_4\cdot 2MeCN$

Solution A

The addition of water to the controlled hydrolysis reactions was effected by syringe injection of the appropriate amount of standard H_2O/MeCN solution (0.00406 g/cm^3); the latter was prepared by the careful addition of H_2O (2.030g, 0.11 mmol) to MeCN in a calibrated 50 cm^3 volumetric flask.

Preparation of $[Mg(MeCN)_6][\{TiCl_4(MeCN)\}_2(\mu\text{-}O)]\cdot 4MeCN$

A solution of $TiCl_4$ (2.13g, 11.229 mmol) in MeCN (25 cm^3) was added dropwise to a suspension of $MgCl_2$ (0.535g, 5.619 mmol) in MeCN (50 cm^3). The mixture was warmed (50°C) and stirred for 5 hours to give a clear yellow solution. On cooling this solution to room temperature hydrolysis was induced by the dropwise addition of solution A (2.50 cm^3, 5.634 mmol) and the resulting deep yellow solution was stirred for a further 24 hours. Slow removal of solvent, to approximately one quarter of the original volume, resulted in the deposition of yellow needle crystals. Yield 1.98g, 38.6%. Anal Calcd for C_{24} H_{36} N_{12} Mg Ti_2Cl_8O: C, 31.60, H, 3.98, N, 18.42, Cl, 31.09. Found: C, 31.39, H, 3.78, N, 18.22, Cl, 29.94%. ν_{max}(CN) 2313m, 2286m, ν_{asym}(Ti-O-Ti) 786, ν(Ti-Cl) 495s, 428s, 405w, 390w, 345vs, (br), 280vw, sh cm^{-1} (Nujol).

Preparation of $[TiCl_2(MeCN)_2(\mu\text{-}O)]_4 \cdot 2MeCN$

The standard solution A (2.00 cm^3, 4.507 mmol) was added dropwise to a chilled (O°C) solution of $TiCl_4$ (1.710g, 9.014 mmol) in MeCN (30 cm^3) and the resulting deep yellow solution stirred at room temperature for 24 hours. Following slow removal of solvent, to approximately one quarter of the original volume, the concentrated solution was placed in the refrigerator where pale yellow needle crystals deposited. Yield, 0.89g, 41.5%. Anal Calcd. for $C_{20}H_{30}N_{10}Ti_4Cl_8O_4$: C, 25.30, H, 3.18, N, 14.75, Cl, 29.87. Found C, 24.98, H, 3.00, N, 14.29, Cl, 29.66%. ν_{max}(CN) 2310m, 2279m, ν_{asym}(Ti-O-Ti) 780, ν(Ti-Cl) 492w, 402sh, 380vs, (br), 330sh, 274s cm^{-1} (Nujol).

EXPERIMENTAL FOR CHAPTER SEVEN

Reaction of *p*-Toluic Acid with $Cp^{*}TiCl_3$

The reagent methyl lithium (1.75cm^3, 1.6M in ether) was added dropwise to a chilled (-75°C) stirred solution of $Cp^{*}TiCl_3$ (0.3g, 0.9 mmol) in hexane (30 cm^3). The reaction mixture was maintained at this temperature for 30 minutes then allowed to warm to room temperature. As the reaction warmed the solution changed from orange to a murky green with the precipitation of lithium chloride. Following the removal of the precipitate a yellow solution remained. The *p*-toluic acid (0.38g, 2.79 mmol) was dissolved in a small amount of ether and transferred to a dropping funnel attached to a bubbler outlet. This solution was added dropwise to the yellow solution (0°C) resulting in an immediate colour change to deep red and finally to brown with the evolution of gas (CH_4). The reaction was allowed to warm to 25°C then concentrated to half the original volume and the precipitate which appeared collected and washed with hexane (3 x 30 cm^3) followed by drying *in vacuo*. The solid was dissolved in toluene (10 cm^3), layered with an equal volume of hexane and placed in a freezer (-12°) for twelve hours during which time pale yellow crystals deposited. The mother liquors were removed and the crystals washed with hexane (3 x 15 cm^3) and dried *in vacuo*. Yield 0.18g, 53%. Anal. Calcd for $C_{42}H_{56}O_6Ti_2$: C, 67.02, H, 7.50. Found: C, 67.37, 7.46, ν_{max} 1609s, 1582m, 1517m, 1490m, 657w, 478s, 351m, 307m, 307m, 281w, 230w cm^{-1} (Nujol). δ (C_6D_6) 1.353 (6H), 1.427 (36H), 6.557-6.565 (8H), 6.759-6.767 (not integrated).

APPENDIX

APPENDIX

Table 51. Crystal Data for $[\{TiCl(\mu\text{-}O)(12\text{-crown-}4)\}_2][SbCl_6]_2 \cdot 2CH_2Cl_2$

Formula	$[C_{16}H_{32}Cl_2O_{10}Ti_2]^{2+}2[SbCl_6]^- \cdot 2CH_2Cl_2$
M	1389.93
Crystal Class	monoclinic
Space Group	$P2_1/n$
a (Å)	8.337(4)
b (Å)	21.307(10)
c (Å)	13.626(8)
β (°)	107.13(4)
V ($Å_3$)	2331
Z	2
Dc (g cm^{-3})	1.90
Mo-Kα radiation	
λ (Å)	0.71069
μ(Mo-Kα)(mm^{-1})	2.57
T (K)	290

Table 52. Selected Bond Lengths (Å) and Angles (°) for

$[\{TiCl(\mu\text{-}O)(12\text{-crown-}4)\}_2][SbCl_6]_2 \cdot 2CH_2Cl_2$

Ti(1)-Cl(1)	2.277)2)	Ti(1)-O(012)	1.811(3)
Ti(1)-O(1)	2.306(4)	Ti(1)-O(4)	2.237(4)
Ti(1)-O(7)	2.303(4)	Ti(1)-O(10)	2.121(4)
Ti(1)...Ti(1a)	2.789(2)	Ti(1)-O(012a)	1.823(4)
O(012)-Ti(1a)	1.823(4)	O(1)-C(2)	1.448(7)
O(1)-C(12)	1.424(8)	C(2)-C(3)	1.472(10)
C(3)-O(4)	1.423(7)	O(4)-C(5)	1.453(8)
C(5)-C(6)	1.486(8)	C(6)-O(7)	1.433(7)
C(7)-C(8)	1.433(7)	C(8)-C(9)	1.513(10)
C(9)-O(10)	1.436(6)	O(10)-C(11)	1.464(8)
C(11)-C(12)	1.498(7)		

Cl(1)-Ti(1)-O(1)	98.3(1)	O(012)-Ti(1)-O(1)	152.4(2)
Cl(1)-Ti(1)-O(4)	82.3(1)	O(012)-Ti(1)-O(4)	138.6(2)
O(1)-Ti(1)-O(4)	66.8(1)	Cl(1)-Ti(1)-O(7)	107.7(1)
O(012)-Ti(1)-O(7)	74.8(1)	O(1)-Ti(1)-O(7)	121.8(1)
O(4)-Ti(1)-O(7)	66.4(1)	Cl(1)-Ti(1)-O(10)	166.8(1)
O(012)-Ti(1)-O(10)	96.1(1)	O(1)-Ti(1)-O(10)	71.6(1)
O(4)-Ti(1)-O(10)	85.8(2)	O(7)-Ti(1)-O(10)	72.3(1)
Cl(1)-Ti(1)-O(012a)	95.9(1)	O(012)-Ti(1)-O(012a)	79.7(2)
O(1)-Ti(1)-O(012a)	75.7(1)	O(4)-Ti(1)-O(012a)	141.7(1)
O(7)-Ti(1)-O(012a)	146.8(1)	O(10)-Ti(1)-O(012a)	89.8(2)

C(2)-O(1)-C(12)	114.7(5)	Ti(1)-O(012)-Ti(1a)	100.3(2)
C(6)-O(7)-C(8)	114.7(4)	C(3)-O(4)-C(5)	118.5(4)
Cl(1)-Ti(1)-O(012)	96.5(1)	C(9)-O(10)-C(11)	113.0(4)

Table 53. Crystal Data for $[SnCl_3(9\text{-}S\text{-}3)]_2[SnCl_6]$

Empirical formula	C4 H8 Cl4 S2 Sn
Formula weight	380.71
Temperature	230(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	Pbca
Unit cell dimensions	a = 11.245(5) Å α = 90°
	b = 12.927(6) Å β = 90°
	c = 23.779(10) Å γ = 90°
Volume	3457(3) Å^3
Z	12
Density (calculated)	2.195 Mg/m^3
Crystal size	0.20 x 0.20 x 0.09 mm

Table 54. Bond Lengths (Å) and Angles (°) for $[SnCl_3(9\text{-}S\text{-}3)]_2[SnCl_6]$

Sn(1)-Cl(2)	2.366(4)
Sn(1)-Cl(3)	2.369(3)
Sn(1)-Cl(1)	2.371(4)
Sn(1)-S(4)	2.618(3)
Sn(1)-S(7)	2.636(3)
Sn(1)-S(1)	2.657(4)
Sn(2)-Cl(6)#1	2.442(4)
Sn(2)-Cl(6)	2.442(4)
Sn(2)-Cl(5)	2.451(4)
Sn(2)-Cl(5)#1	2.451(4)
Sn(2)-Cl(4)#	2.451(3)
Sn(2)-Cl(4)	2.451(3)
S(1)-C(9)	1.838(11)
S(1)-C(2)	1.840(12)
S(4)-C(3)	1.843(14)
S(4)-C(5)	1.848(12)
S(7)-C(6)	1.834(13)
S(7)-C(8)	1.84(2)
C(2)-C(3)	1.50(2)
C(5)-C(6)	1.53(2)
C(8)-C(9)	1.58(2)
Cl(2)-Sn(1)-Cl(3)	98.79(13)
Cl(2)-Sn(1)-Cl(1)	101.38(13)

Cl(3)-Sn(1)-Cl(1)	95.40(13)
Cl(2)-Sn(1)-S(4)	86.93(12)
Cl(3)-Sn(1)-S(4)	86.97(12)
Cl(1)-Sn(1)-S(4)	170.87(14)
Cl(2)-Sn(1)-S(7)	86.76(12)
Cl(3)-Sn(1)-S(7)	169.60(12)
Cl(1)-Sn(1)-S(7)	92.10(13)
S(4)-Sn(1)-S(7)	84.54(11)
Cl(2)-Sn(1)-S(1)	165.88(12)
Cl(3)-Sn(1)-S(1)	90.01(12)
Cl(1)-Sn(1)-S(1)	88.67(13)
S(4)-Sn(1)-S(1)	82.51(11)
S(7)-Sn(1)-S(1)	82.94(11)
Cl(6)#1-Sn(2)-Cl(6)	180.0(12)
Cl(6)#1-Sn(2)-Cl(5)	89.83(13)
Cl(6)-Sn(2)-Cl(5)	90.17(13)
Cl(6)#1-Sn(2)-Cl(5)#1	90.17(13)
Cl(6)-Sn(2)-Cl(5)#1	89.83(13)
Cl(5)-Sn(2)-Cl(5)#1	179.997(1)
Cl(6)#1-Sn(2)-Cl(4)#1	89.84(12)
Cl(6)-Sn(2)-Cl(4)#1	90.16(12)
Cl(5)-Sn(2)-Cl(4)#1	91.17(11)
Cl(5)#1-Sn(2)-Cl(4)#1	88.83(11)
Cl(6)#1-Sn(2)-Cl(4)	90.17(12)

Cl(6)-Sn(2)-Cl(4)	89.83(12)
Cl(5)-Sn(2)-Cl(4)	88.83(11)
Cl(5)#1-Sn(2)-Cl(4)	91.17(11)
Cl(4)#1-Sn(2)-Cl(4)	180.0
C(9)-S(1)-C(2)	105.1(6)
C(9)-S(1)-Sn(1)	99.8(5)
C(2)-S(1)-Sn(1)	103.2(4)
C(3)-S(4)-C(5)	102.9(6)
C(3)-S(4)-Sn(1)	99.6(5)
C(5)-S(4)-Sn(1)	102.3(4)
C(6)-S(7)-C(8)	103.2(6)
C(6)-S(7)-Sn(1)	96.3(4)
C(8)-S(7)-Sn(1)	104.8(4)
C(3)-C(2)-S(1)	115.6(9)
C(2)-C(3)-S(4)	116.4(8)
C(6)-C(5)-S(4)	113.4(9)
C(5)-C(6)-S(7)	117.4(9)
C(9)-C(8)-S(7)	114.7(9)
C(8)-C(9)-S(1)	116.7(9)

Table 55. Crystal Data for $2(SnCl_4)\cdot 18\text{-}S\text{-}6$

Empirical formula	C14 H24 Cl8 N S6 Sn2
Formula weight	919.68
Temperature	240(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C2
Unit cell dimensions	a = 16.901(5) Å α = 90°
	b = 12.968(5) Å β = 100.50(3)°
	c = 7.284(3) Å γ = 90°
Volume	1569.7(10) $Å^3$
Z	2
Density (calculated)	1.946 Mg/m^3
Crystal size	0.14 x 0.13 x 0.07 mm

Table 56. Bond Lengths (Å) and Angles (°) for 2($SnCl_4$)·18-S-6.

Sn(1)-Cl(3')	2.30(2)
Sn(1)-Cl(4)	2.31(2)
Sn(1)-Cl(3)	2.38(2)
Sn(1)-Cl(2)	2.391(2)
Sn(1)-Cl(1)	2.421(2)
Sn(1)-Cl(4')	2.42(2)
Sn(1)-S(4)	2.535(10)
Sn(1)-S(7')	2.56(2)
Sn(1)-S(7)	2.687(13)
Sn(1)-S(4')	2.689(13)
S(1)-C(2)	1.81(2)
S(1)-C(2')#1	1.93(4)
C(2)-C(3)	1.64(3)
C(2')-C(3)	1.61(2)
C(2')-S(1)#1	1.93(4)
C(3)-S(4)	1.81(2)
C(3)-S(4')	1.98(2)
S(4)-C(5)	1.80(2)
C(5)-C(6)	1.48(2)
C(6)-S(7)	1.85(3)
S(7)-C(8)	1.87(2)
S(7')-C(8)	1.68(3)
C(8)-C(9')	1.60(3)

C(8)-C(9)	1.68(2)
C(9)-S(10)	1.82(2)
S(10)-C(9')#1	1.72(5)
C(9')-S(10)#1	1.72(5)
N(21)-C(21)	1.11(3)
C(21)-C(22)	1.61(4)
N(31)-C(31)	1.13(2)
C(31)-C(32)	1.56(2)

Cl(4)-Sn(1)-Cl(3)	97.3(7)
Cl(3')-Sn(1)-Cl(2)	97.6(5)
Cl(4)-Sn(1)-Cl(2)	96.7(5)
Cl(3)-Sn(1)-Cl(2)	91.5(5)
Cl(3')-Sn(1)-Cl(1)	91.8(5)
Cl(4)-Sn(1)-Cl(1)	93.2(5)
Cl(3)-Sn(1)-Cl(1)	94.3(5)
Cl(2)-Sn(1)-Cl(1)	167.85(8)
Cl(3')-Sn(1)-Cl(4')	97.8(7)
Cl(2)-Sn(1)-Cl(4')	93.0(5)
Cl(1)-Sn(1)-Cl(4')	93.3(5)
Cl(4)-Sn(1)-S(4)	92.1(7)
Cl(3)-Sn(1)-S(4)	169.4(6)
Cl(2)-Sn(1)-S(4)	82.6(4)
Cl(1)-Sn(1)-S(4)	90.0(4)

Cl(3')-Sn(1)-S(7')	91.5(8)
Cl(2)-Sn(1)-S(7')	81.9(5)
Cl(1)-Sn(1)-S(7')	90.2(5)
Cl(4')-Sn(1)-S(7')	170.0(8)
Cl(4)-Sn(1)-S(7)	175.8(8)
Cl(3)-Sn(1)-S(7)	86.8(7)
Cl(2)-Sn(1)-S(7)	82.0(4)
Cl(1)-Sn(1)-S(7)	87.7(4)
S(4)-Sn(1)-S(7)	83.8(5)
Cl(3')-Sn(1)-S(4')	175.8(7)
Cl(2)-Sn(1)-S(4')	81.6(4)
Cl(1)-Sn(1)-S(4')	88.4(4)
Cl(4')-Sn(1)-S(4')	86.3(7)
S(7')-Sn(1)-S(4')	84.4(7)
C(3)-C(2)-S(1)	114(2)
C(3)-C(2')-S(1)#1	102(2)
C(2)-C(3)-S(4)	102(2)
C(2')-C(3)-S(4')	101(2)
C(5)-S(4)-C(3)	95.3(12)
C(5)-S(4)-Sn(1)	101.8(7)
C(3)-S(4)-Sn(1)	114.4(11)
C(6)-C(5)-S(4)	113.7(11)
C(5)-C(6)-S(7)	113.0(9)
C(6)-S(7)-C(8)	110.7(14)

C(6)-S(7)-Sn(1)	95.0(9)
C(8)-S(7)-Sn(1)	103.0(11)
C(3)-S(4')-Sn(1)	102.8(10)
C(8)-S(7')-Sn(1)	114.7(13)
C(9')-C(8)-S(7')	120(2)
C(9)-C(8)-S(7)	132(2)
C(8)-C(9)-S(10)	114(2)
C(8)-C(9')-S(10)#1	113(3)
N(21)-C(21)-C(22)	180.000(3)
N(31)-C(31)-C(32)	180.00(2)

Table 57. Crystal Data for $[Mg(MeCN)_6][\{TiCl_4(MeCN)\}_2(\mu\text{-}O)]\cdot 4MeCN$

Empirical Formula	C24 H36 C18 Mg N12 O Ti2
Formula weight	912.36
Temperature (K)	293
Wavelength (Å)	0.71071
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell dimensions (Å)	a = 14.777(6)
	b = 14.603(6)
	c = 21.214(10)
(°)	β = 105.3(1)
Volume ($Å^3$)	4415
Z	4
Density (calculated)(Mg/m^3)	1.373
Absorbtion coefficient (mm^{-1})	0.895
F(000)	1856

Table 58. Selected Bond Lengths (Å) and Angles (°) in $[Mg(MeCN)_6][\{TiCl_4(MeCN)_2\}(\mu\text{-}O)]\cdot 4MeCN$

Ti(1)-O(1)	1.783(4)
Ti(1)-N(11)	2.273(5)
Ti(1)-Cl(11)	2.316(2)
Ti(1)-Cl(12)	2.296(2)
Ti(1)-Cl(13)	2.318(2)
Ti(1)-Cl(14)	2.323(2)
Ti(2)-O(1)	1.764(4)
Ti(2)-N(21)	2.278(5)
Ti(2)-Cl(21)	2.314(2)
Ti(2)-Cl(22)	2.306(2)
Ti(2)-Cl(23)	2.318(2)
Ti(2)-Cl(24)	2.316(2)
O(1)-Ti(1)-N(11)	178.5(2)
O(1)-Ti(1)-Cl(12)	95.08(14)
N(11)-Ti(1)-Cl(12)	83.7(2)
O(1)-Ti(1)-Cl(11)	95.54(13)
N(11)-Ti(1)-Cl(11)	83.54(14)
Cl(12)-Ti(1)-Cl(11)	90.93(8)
O(1)-Ti(1)-Cl(13)	96.00(14)
N(11)-Ti(1)-Cl(13)	84.95(14)
Cl(12)-Ti(1)-Cl(13)	89.17(7)

Cl(11)-Ti(1)-Cl(13)	168.41(8)
O(1)-Ti(1)-Cl(14)	97.2(2)
N(11)-Ti(1)-Cl(14)	84.0(2)
Cl(12)-Ti(1)-Cl(14)	167.62(9)
Cl(11)-Ti(1)-Cl(14)	89.18(7)
Cl(13)-Ti(1)-Cl(14)	88.25(7)
O(1)-Ti(2)-N(21)	177.0(2)
O(1)-Ti(2)-Cl(22)	98.1(2)
N(21)-Ti(2)-Cl(22)	84.5(2)
O(1)-Ti(2)-Cl(21)	96.43(14)
2N(21)-Ti(2)-Cl(21)	85.0(2)
Cl(22)-Ti(2)-Cl(21)	89.62(7)
O(1)-Ti(2)-Cl(24)	95.3(2)
N(21)-Ti(2)-Cl(24)	82.0(2)
Cl(22)-Ti(2)-Cl(24)	166.54(9)
Cl(21)-Ti(2)-Cl(24)	89.19(7)
O(1)-Ti(2)-Cl(23)	95.19(14)
N(21)-Ti(2)-Cl(23)	83.4(2)
Cl(22)-Ti(2)-Cl(23)	89.08(7)
Cl(21)-Ti(2)-Cl(23)	168.37(8)
Cl(24)-Ti(2)-Cl(23)	89.40(8)
Ti(2)-O(1)-Ti(1)	174.7(3)

Magnesium Environment

Mg(3)-N(31)	2.129(6)
Mg(3)-N(51)	2.131(7)
Mg(3)-N(61)	2.141(7)
Mg(3)-N(41)	2.154(7)
Mg(3)-N(81)	2.165(7)
Mg(3)-N(71)	2.184(7)
N(31)-Mg(3)-N(51)	177.4(3)
N(31)-Mg(3)-N(61)	91.3(2)
N(51)-Mg(3)-N(61)	90.6(3)
N(31)-Mg(3)-N(41)	89.4(3)
N(51)-Mg(3)-N(41)	88.7(3)
N(61)-Mg(3)_N(41)	178.3(2)
N(31)-Mg(3)-N(81)	90.2(3)
N(51)-Mg(3)-N(81)	91.5(3)
N(61)-Mg(3)-N(81)	91.9(2)
N(41)-Mg(3)-N(81)	86.6(3)
N(31)-Mg(3)-N(71)	91.4(2)
N(51)-Mg(3)-N(71)	86.9(2)
N(61)-Mg(3)-N(71)	87.2(2)
N(41)-Mg(3)-N(71)	94.3(3)
N(81)-Mg(3)-N(71)	178.2(3)

Remaining Dimensions in Anion

N(21)-C(22)	1.092(9)
C(22)-C(23)	1.466(10)
N(11)-C(12)	1.099(8)
C(12)-C(13)	1.448(9)
C(22)-N(21)-Ti(2)	174.6(6)
N(21)-C(22)-C(23)	178.1(8)
C(12)-N(11)-Ti(1)	176.9(5)
N(11)-C(12)-C(13)	177.9(8)

Remaining Dimensions in Cation

N(31)-C(32)	1.119(9)
C(32)-C(33)	1.431(10)
N(41)-C(42)	1.128(9)
C(42)-C(43)	1.452(10)
N(51)-C(52)	1.113(9)
C(52)-C(53)	1.445(11)
N(61)-C(62)	1.119(9)
C(62)-C(63)	1.450(10)
N(71)-C(72)	1.117(9)
C(72)-C(73)	1.457(11)
N(81)-C(82)	1.115(9)
C(82)-C(83)	1.458(10)
C(32)-N(31)-Mg(3)	171.2(6)

N(31)-C(32)-C(33)	178.5(8)
C(42)-N(41)-Mg(3)	167.2(6)
N(41)-C(42)-C(43)	178.6(8)
C(52)-N(51)-Mg(3)	171.5(7)
N(51)-C(52)-C(53)	179.1(8)
C(62)-N(61-Mg(3)	173.4(6)
N(61)-C(62)-C(63)	179.7(7)
C(72)-N(71)-Mg(3)	166.9(6)
N(71)-C(72)-C(73)	178.8(8)
C(82)-N(81)-Mg(3)	170.9(6)
N(81)-C(82)-C(83)	179.1(8)

Solvent molecules

N(84)-C(85)	1.124(13)
C(85)-C(86)	1.403(14)
N(87)-C(88)	1.104(13)
C(88)-C(89)	1.404(14)
N(91)-C(92)	1.108(12)
C(92)-C(93)	1.410(14)
N(94)-C(95)	1.116(12)
C(95)-C(96)	1.419(13)
N(84)-C(85)-C(86)	178.(14)
N(87)-C(88)-C(89)	179(2)
N(91)-C(92)-C(93)	177.5(12)
N(94)-C(95)-C(96)	179.9(12)

Table 59. Crystal Data for $[TiCl_2(MeCN)_2(\mu\text{-}O)]_4$

Empirical Formula	C20 H30 C18 N10 O4 Ti4
Formula weight	949.69
Temperature (K)	293
Wavelength (A)	0.71071
Crystal system	orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions (Å)	a = 12.165(6)
	b = 12.367(6)
	c = 27.927(11)
Volume ($Å^3$)	4202
Z	8
Density (calculated) (Mg/m^3)	1.492
Absorbtion coefficient (mm^{-1})	1.279
F(000)	1880

Table 60. Selected Bond Lengths (Å) and Angles (°) in $[TiCl_2(MeCN)_2(\mu\text{-}O)]_4$

Ti(1)-O(4)	1.664(10)
Ti(1)-O(1)	1.936(10)
Ti(1)-N(11)	2.166(14)
Ti(1)-Cl(12)	2.287(5)
Ti(1)-Cl(11)	2.323(4)
Ti(1)-N(12)	2.356(13)
Ti(2)-O(1)	1.683(10)
Ti(2)-O(2)	1.960(10)
Ti(2)-N(21)	2.168(12)
Ti(2)-N(22)	2.305(12)
Ti(2)-Cl(22)	2.295(5)
Ti(2)-Cl(21)	2.329(4)
Ti(3)-O(2)	1.672(10)
Ti(3)-O(3)	1.967(9)
Ti(3)-N(31)	2.207(13)
Ti(3)-Cl(32)	2.285(4)
Ti(3)-N(32)	2.314(14)
Ti(3)-Cl(31)	2.341(4)
Ti(4)-O(3)	1.653(9)
Ti(4)-O(4)	1.954(10)
Ti(4)-N(41)	2.191(14)
Ti(4)-Cl(42)	2.280(5)

Ti(4)-Cl(41)	2.334(4)
Ti(4)-N(42)	2.336(12)
O(4)-Ti(1)-O(1)	97.6(4)
O(4)-Ti(1)-N(11)	89.3(5)
O(1)-Ti(1)-N(11)	80.1(5)
O(4)-Ti(1)-Cl(12)	99.9(4)
O(1)-Ti(1)-Cl(12)	94.5(4)
N(11)-Ti(1)-Cl(12)	170.0(4)
O(4)-Ti(1)-Cl(11)	99.2(3)
O(1)-Ti(1)-Cl(11)	158.6(3)
N(11)-Ti(1)-Cl(11)	87.0(4)
Cl(12)-Ti(1)-Cl(11)	95.5(2)
O(4)-Ti(1)-N(12)	171.2(5)
O(1)-Ti(1)-N(12)	78.2(4)
N(11)-Ti(1)-N(12)	82.3(5)
Cl(12)-Ti(1)-N(12)	88.3(4)
Cl(11)-Ti(1)-N(12)	83.2(4)
O(1)-Ti(2)-O(2)	97.9(4)
O(1)-Ti(2)-N-(21)	92.0(5)
O(2)-Ti(2)-N(21)	82.5(4)
O(1)-Ti(2)-N(22)	172.0(5)
O(2)-Ti(2)-N(22)	79.7(4)
N(22)-Ti(2)-N(21)	80.1(5)
O(1)-Ti(2)-Cl(22)	100.5(4)

O(2)-Ti(2)-Cl(22)	94.1(3)
N(21)-Ti(2)-Cl(22)	167.4(4)
N(22)-Ti(2)-Cl(22)	87.3(4)
O(1)-Ti(2)-Cl(21)	96.5(3)
O(2)-Ti(2)-Cl(21)	161.6(3)
N(21)-Ti(2)-Cl(21)	85.7(4)
N(22)-Ti(2)-Cl(21)	84.5(3)
Cl(22)-Ti(2)-Cl(21)	94.4(2)
O(2)-Ti(3)-O(3)	97.8(4)
O(2)-Ti(3)-N(31)	90.2(5)
O(3)-Ti(3)-N(31)	82.0(4)
O(2)-Ti(3)-Cl(32)	101.3(4)
O(3)-Ti(3)-Cl(32)	91.9(3)
N(31)-Ti(3)-Cl(32)	167.6(4)
O(2)-Ti(3)-N(32)	169.1(5)
O(3)-Ti(3)-N(32)	78.5(4)
N(31)-Ti(3)-N(32)	79.2(5)
Cl(32)-Ti(3)-N(32)	89.1(4)
O(2)-Ti(3)-Cl(31)	98.8(3)
O(3)-Ti(3)-Cl(31)	160.3(3)
N(31)-Ti(3)-Cl(31)	87.4(3)
Cl(32)-Ti(3)-Cl(31)	95.1(2)
N(32)-Ti(3)-Cl(31)	83.3(4)
O(4)-Ti(4)-O(3)	98.2(4)

O(3)-Ti(4)-N(41)	89.8(5)
O(4)-Ti(4)-N(41)	81.5(4)
O(3)-Ti(4)-Cl(42)	99.1(4)
O(4)-Ti(4)-Cl(42)	94.2(3)
N(41)-Ti(4)-Cl(42)	170.6(4)
O(3)-Ti(4)-Cl(41)	98.9(3)
O(4)-Ti(4)-Cl(41)	158.9(3)
N(41)-Ti(4)-Cl(41)	86.2(3)
Cl(42)-Ti(4)-Cl(41)	95.3(2)
O(3)-Ti(4)-N(42)	172.4(5)
O(4)-Ti(4)-N(42)	77.4(4)
N(41)-Ti(4)-N(42)	83.4(5)
Cl(42)-Ti(4)-N(42)	87.5(4)
Cl(41)-Ti(4)-N(42)	84.2(3)
Ti(2)-O(1)-Ti(1)	172.3(5)
Ti(3)-O(2)-Ti(2)	166.8(6)
Ti(4)-O(3)-Ti(3)	172.6(5)
Ti(1)-O(4)-Ti(4)	168.5(6)
N(11)-C(111)	1.06(2)
C(111)-C(112)	1.52(3)
N(12)-C(121)	1.09(2)
C(121)-C(122)	1.45(2)
N(22)-C(221)	1.09(2)
C(221)-C(222)	1.50(2)

N(21)-C(211)	1.10(2)
C(211)-C(212)	1.46(3)
N(31)-C(311)	1.14(2)
C(311)-C(312)	1.41(3)
N(32)-C(321)	1.08(2)
C(321)-C(322)	1.54(3)
N(41)-C(411)	1.12(2)
C(411)-C(412)	1.46(3)
N(42)-C(421)	1.11(2)
C(421)-C(422)	1.45(2)
C(100)-C(101)	1.35(5)
C(101)-N(102)	1.16(5)
N(103)-C(104)	1.20(6)
C(104)-C(105)	1.32(6)
C(111)-N(11)-Ti(1)	155.4(14)
N(11)-C(111)-C(112)	74(2)
C(121)-N-(12)-Ti(1)	62.7(13)
N(12)-C(121)-C(122)	177(2)
C(211)-N(21)-Ti(2)	173.3(13)
N(21)-C-(211)-C(212)	177(2)
C(221)-N-(22)-Ti(2)	162.5(14)
N(22)-C-(221)-C(222)	166(3)
C(311)-N-(31)-Ti(3)	163.7(12)
N(31)-C(311)-C(312)	179(2)

C(321)-N-(32)-Ti(3)	164.3(14)
N(32)-C-(321)-C(322)	176(3)
C(411)-N-(41)-Ti(4)	161.5(13)
N(41)-C(411)-C(412)	178(2)
C(421)-N(42)-Ti(4)	155.8(14)
N(42)-C(421)-C(422)	177(2)
N(102)-C(101)-C(100)	172(5)
N(103)-C(104)-C(105)	157(6)

Table 61. Crystal Data for $[Cp''Ti(O_2CPhMe)(\mu\text{-}O)]_2$

Empirical formula	$C_{21}H_{28}O_3Ti$
Formula weight	376.33
Temperature	240(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/c
Unit cell dimensions	a = 10.762(4) Å α = 90°
	b = 15.029(5) Å β = 107.91(3)°
	c = 13.065(4) Å γ = 90°
Volume	2010.8(12) $Å^3$
Z	4
Density (calculated)	1.243 Mg/m^3
Crystal size	0.28 x 0.26 x 0.13 mm

Table 62. Bond Lengths (Å) and Angles (°) for [Cp"Ti(O_2CPhMe)(μ-O)]$_2$

Ti(1)-O(3)#1	1.822(4)
Ti(1)-O(3)	1.845(4)
Ti(1)-O(1)#1	2.116(4)
Ti(1)-O(2)#1	2.133(4)
Ti(1)-C(25)#1	2.341(6)
Ti(1)-C(22)#1	2.368(6)
Ti(1)-C(21)#1	2.370(6)
Ti(1)-C(23)#1	2.378(6)
Ti(1)-C(24)#1	2.397(6)
Ti(1)-C(11)#1	2.491(6)
Ti(1)-Ti(1)#1	2.742(3)
O(1)-C(11)	1.276(7)
O(1)-Ti(1)#1	2.116(4)
O(2)-C(11)	1.270(7)
O(2)-Ti(1)#1	2.133(4)
O(3)-Ti(1)#1	1.822(4)
C(11)-C(12)	1.479(8)
C(11)-Ti(1)#1	2.491(6)
C(12)-C(13)	1.349(8)
C(12)-C(18)	1.361(8)
C(13)-C(14)	1.396(8)
C(14)-C(15)	1.366(9)
C(15)-C(17)	1.357(9)

C(15)-C(16)	1.511(9)
C(17)-C(18)	1.388(8)
C(21)-C(25)	1.392(8)
C(21)-C(22)	1.401(8)
C(21)-C(31)	1.524(9)
C(21)-Ti(1)#1	2.370(6)
C(22)-C(23)	1.410(8)
C(22)-Ti(1)#1	2.368(6)
C(23)-C(24)	1.395(8)
C(23)-Ti(1)#1	2.378(6)
C(24)-C(25)	1.410(8)
C(24)-C(41)	1.527(9)
C(24)-Ti(1)#1	2.397(6)
C(25)-Ti(1)#1	2.341(6)
C(31)-C(32)	1.525(8)
C(31)-C(34)	1.536(8)
C(31)-C(33)	1.538(8)
C(41)-C(42)	1.520(8)
C(41)-C(44)	1.544(8)
C(41)-C(43)	1.544(8)
O(3)#1-Ti(1)-O(3)	83.2(2)
O(3)#1-Ti(1)-O(1)#1	127.0(2)
O(3)-Ti(1)-O(1)#1	87.9(2)
O(3)#1-Ti(1)-O(2)#1	87.5(2)

O(3)-Ti(1)-O(2)#1	131.9(2)
O(1)#1-Ti(1)-O(2)#1	61.3(2)
O(3)#1-Ti(1)-C(25)#1	94.4(2)
O(3)-Ti(1)-C(25)#1	95.9(2)
O(1)#1-Ti(1)-C(25)#1	138.5(2)
O(2)#1-Ti(1)-C(25)#1	131.9(2)
O(3)#1-Ti(1)-C(22)#1	117.7(2)
O(3)-Ti(1)-C(22)#1	144.3(2)
O(1)#1-Ti(1)-C(22)#1	99.1(2)
O(2)#1-Ti(1)-C(22)#1	80.4(2)
C(25)#1-Ti(1)-C(22)#1	56.4(2)
O(3)#1-Ti(1)-C(21)#1	89.3(2)
O(3)-Ti(1)-C(21)#1	129.0(2)
O(1)#1-Ti(1)-C(21)#1	133.5(2)
O(2)#1-Ti(1)-C(21)#1	97.8(2)
C(25)#1-Ti(1)-C(21)#1	34.4(2)
C(22)#1-Ti(1)-C(21)#1	34.4(2)
O(3)#1-Ti(1)-C(23)#1	146.7(2)
O(3)-Ti(1)-C(23)#1	113.3(2)
O(1)#1-Ti(1)-C(23)#1	83.8(2)
O(2)#1-Ti(1)-C(23)#1	99.9(2)
C(25)#1-Ti(1)-C(23)#1	56.7(2)
C(22)#1-Ti(1)-C(23)#1	34.6(2)
C(21)#1-Ti(1)-C(23)#1	57.7(2)

O(3)#1-Ti(1)-C(24)#1	126.7(2)
O(3)-Ti(1)-C(24)#1	87.4(2)
O(1)#1-Ti(1)-C(24)#1	104.8(2)
O(2)#1-Ti(1)-C(24)#1	133.4(2)
C(25)#1-Ti(1)-C(24)#1	34.6(2)
C(22)#1-Ti(1)-C(24)#1	56.9(2)
C(21)#1-Ti(1)-C(24)#1	57.8(2)
C(23)#1-Ti(1)-C(24)#1	34.0(2)
O(3)#1-Ti(1)-C(11)#1	107.4(2)
O(3)-Ti(1)-C(11)#1	110.2(2)
O(1)#1-Ti(1)-C(11)#1	30.8(2)
O(2)#1-Ti(1)-C(11)#1	30.6(2)
C(25)#1-Ti(1)-C(11)#1	147.4(2)
C(22)#1-Ti(1)-C(11)#1	91.6(2)
C(21)#1-Ti(1)-C(11)#1	120.2(2)
C(23)#1-Ti(1)-C(11)#1	94.1(2)
C(24)#1-Ti(1)-C(11)#1	125.0(2)
O(3)#1-Ti(1)-Ti(1)#1	41.92(13)
O(3)-Ti(1)-Ti(1)#1	41.28(12)
O(1)#1-Ti(1)-Ti(1)#1	112.03(14)
O(2)#1-Ti(1)-Ti(1)#1	114.84(14)
C(25)#1-Ti(1)-Ti(1)#1	96.9(2)
C(22)#1-Ti(1)-Ti(1)#1	148.9(2)
C(21)#1-Ti(1)-Ti(1)#1	114.5(2)

C(23)#1-Ti(1)-Ti(1)#1	145.3(2)
C(24)#1-Ti(1)-Ti(1)#1	111.5(2)
C(11)#1-Ti(1)-Ti(1)#1	115.5(2)
C(11)-O(1)-Ti(1)#1	91.0(4)
C(11)-O(2)-Ti(1)#1	90.5(4)
Ti(1)#1-O(3)-Ti(1)	96.8(2)
O(2)-C(11)-O(1)	116.7(6)
O(2)-C(11)-C(12)	121.9(6)
O(1)-C(11)-C(12)	121.4(6)
O(2)-C(11)-Ti(1)#1	58.9(3)
O(1)-C(11)-Ti(1)#1	58.2(3)
C(12)-C(11)-Ti(1)#1	174.0(4)
C(13)-C(12)-C(18)	119.4(6)
C(13)-C(12)-C(11)	121.0(6)
C(18)-C(12)-C(11)	119.6(6)
C(12)-C(13)-C(14)	120.5(7)
C(15)-C(14)-C(13)	120.2(7)
C(17)-C(15)-C(14)	118.9(8)
C(17)-C(15)-C(16)	121.4(7)
C(14)-C(15)-C(16)	119.7(7)
C(15)-C(17)-C(18)	120.6(7)
C(12)-C(18)-C(17)	120.4(7)
C(25)-C(21)-C(22)	105.7(6)
C(25)-C(21)-C(31)	128.1(6)

C(22)-C(21)-C(31)	126.0(6)
C(25)-C(21)-Ti(1)#1	71.7(4)
C(22)-C(21)-Ti(1)#1	72.7(4)
C(31)-C(21)-Ti(1)#1	123.6(4)
C(21)-C(22)-C(23)	109.2(6)
C(21)-C(22)-Ti(1)#1	72.9(4)
C(23)-C(22)-Ti(1)#1	73.1(4)
C(24)-C(23)-C(22)	108.2(5)
C(24)-C(23)-Ti(1)#1	73.8(4)
C(22)-C(23)-Ti(1)#1	72.3(3)
C(23)-C(24)-C(25)	106.1(6)
C(23)-C(24)-C(41)	125.9(6)
C(25)-C(24)-C(41)	127.8(6)
C(23)-C(24)-Ti(1)#1	72.3(4)
C(25)-C(24)-Ti(1)#1	70.5(4)
C(41)-C(24)-Ti(1)#1	125.8(4)
C(21)-C(25)-C(24)	110.8(6)
C(21)-C(25)-Ti(1)#1	74.0(4)
C(24)-C(25)-Ti(1)#1	74.9(4)
C(21)-C(31)-C(32)	111.0(6)
C(21)-C(31)-C(34)	112.1(5)
C(32)-C(31)-C(34)	108.5(6)
C(21)-C(31)-C(33)	107.3(5)
C(32)-C(31)-C(33)	109.3(6)

C(34)-C(31)-C(33)	108.6(6)
C(42)-C(41)-C(24)	112.4(6)
C(42)-C(41)-C(44)	109.2(6)
C(24)-C(41)-C(44)	111.2(6)
C(42)-C(41)-C(43)	109.1(6)
C(24)-C(41)-C(43)	105.7(6)
C(44)-C(41)-C(43)	109.1(6)

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